NBS TECHNICAL NOTE 621

Liquid-Vapor Equilibrium in the Binary Systems of He^4 and He^3 with nD_2 and nH_2

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Liquid-Vapor Equilibrium in the Binary Systems of He^4 and He^3 with nD_2 and nH_2

M. J. Hiza

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

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NOMENCLATURE

A, B, C	=	constants of the Antoine equation (eq. 1)
f	=	fugacity
H^{∞}	=	infinite dilution Henry's law constant
ΔH_s	=	heat of solution
K	=	ratio of the mole fraction of a component in the vapor to its mole fraction in the liquid
P	=	pressure
$\bar{P}$	=	partial pressure
P^*	=	reference pressure (1 atm = 0.101325 MN/m^2)
p_o	=	vapor pressure
R	=	gas constant
T	=	absolute temperature, Kelvin
ΔU	=	change in internal energy from a specific state to the ideal gas state
v	=	molar volume
$\bar{v}$	=	partial molar volume
x	=	mole fraction in the liquid phase
y	=	mole fraction in the vapor phase

Greek Letters

δ	=	solubility parameter, $(\Delta U/v)^{1/2}$
π	=	isometric mixing pressure
φ	=	volume fraction, $x_1 v_1/(x_1 v_1 + x_2 v_2)$

Subscripts

1	=	less volatile component (e.g., H_2)
2	=	more volatile component (e.g., He)
nbp	=	normal boiling point
B	=	barotropic

Liquid-Vapor Equilibrium in the Binary Systems of He^4 and He^3 with nD_2 and nH_2*

M. J. Hiza

Cryogenics Division
Institute for Basic Standards, National Bureau of Standards
Boulder, Colorado

Abstract

Experimental data are reported for the equilibrium liquid and vapor phase compositions of the He^4-nD_2 and He^3-nD_2 systems from 20 to 30 K and the He^4-nH_2 and He^3-nH_2 systems from 20 to 28 K. The maximum experimental pressures were 20 and 16 atm (2.0 and 1.6 MN/m^2) for the He^4 and He^3 systems, respectively. In addition, vapor pressures were measured from 20 to 34 K for nD_2 and from 20 to 30 K for nH_2.

Values of Henry's constants, enhancement factors, K-values, and heats of solution were derived from the experimental data for each system. The derived properties are compared with those derived from previous data for the He^4-nH_2, He^4-pH_2, and He^3-nH_2 systems.

Key Words: Binary systems, gas solubility, He^4-nD_2, He^3-nD_2, He^4-nH_2, He^3-nH_2, liquid-vapor equilibrium, nD_2 vapor pressure, nH_2 vapor pressure.

1. Introduction

The purpose of the present investigation was to obtain a consistent set of experimental data on the equilibrium distribution of He^4 and He^3 between the liquid and vapor phases of nD_2 and nH_2. It is hoped that this information will help resolve some of the discrepancies of the earlier investigations on the He^4-H_2 system and also provide additional information for evaluation of predictive methods for systems composed of the molecular species exhibiting strong quantum effects.

In a recent review paper,[1] a detailed discussion was given on the contribution of consistent sets of phase equilibrium data on binary systems of cryogenic interest, and related pure fluid data, to an improvement of prediction methods for mixture properties. The subsequent paper of Sikora[2] is an excellent example of related advancement in fundamental theory. Though the emphasis in both was on systems containing He, H_2, and Ne as one component, the systems and regions covered allowed simplified theoretical treatment. However, theory becomes considerably more complicated and uncertain for binary systems, such as He-Ne, Ne-H_2, and He-H_2, with the various isotopic modifications, in which one or

* This study was carried out at the National Bureau of Standards under the sponsorship of the U. S. Atomic Energy Commission.

both components exhibit strong quantum effects. Reliable experimental data representative of each type of the three systems is indispensible to the theoretical development.

The liquid-vapor equilibrium data for the Ne-nH_2 system of Streett and Jones[3] and Heck and Barrick[4] together cover the liquid range of Ne and are in excellent agreement[5] where comparisons can be made. Similarly, the Ne-nD_2 data of Streett[6] appear to be internally consistent and are in qualitative agreement with the Ne-nH_2 data.[5] The He^4-Ne system was investigated by Heck and Barrick[7] over the entire Ne liquid range up to 200 atm (20 MN/m^2). Subsequent measurements reported by Knorn[8] between the triple point and boiling point temperatures of Ne up to 50 atm (5 MN/m^2) qualitatively confirm the Heck and Barrick data, but do not appear to be as consistent. Nevertheless, the data for the Ne-nH_2, Ne-nD_2, and He^4-Ne systems are reasonably complete and consistent.

Several investigators determined the equilibrium distribution of He^4 between the liquid and vapor phases of nH_2[9, 10, 11] and pH_2.[12, 13] In addition, some measurements were made to determine the three phase locus (S-L-V)[11, 14] and the barotropic locus,[11] i.e., the density inversion locus of the liquid and vapor phases. Observation of the barotropic effect was first reported by H. Kamerlingh Onnes in 1906.[15]

Matyash, Mank, and Starkov[16] report the only data for the solubility of He^3 in liquid H_2. These data provide essentially one isotherm at 20.4 K up to 9.2 atm (0.92 MN/m^2) He^3 partial pressure with a few points at higher and lower temperatures to indicate temperature dependence. There are no published liquid-vapor equilibrium data for the He^4-D_2 and He^3-D_2 systems.

The most significant discrepancy in the He-H_2 systems data is found in the data for the liquid phase. The data of Roellig and Giese,[12] comprised of nine independent data points, suggest that the solubility of He in liquid H_2 decreases with increasing temperature at constant He partial pressure. The only other data available at the time of the above investigation were those of Smith,[9] which indicated the opposite temperature dependence. In addition, the liquid phase He compositions of Roellig and Giese are as much as an order of magnitude larger than those of Smith.

Eckert and Prausnitz[17] showed that the temperatures reported by Roellig and Giese could be in error by as much as 2.7 K, although this correction does not alter the above disagreement. In an attempt to assess the plausibility of each set of discrepant data, Corruccini[18] compared the He K-values and derived heats of solution from each set of data with the corresponding solubility properties deduced from theory, and concluded that the data of Roellig and Giese must be invalid. Corruccini also noted that consistency tests operating solely on the hydrogen fugacities, i.e., the method used by Brazinsky and Gottried[19] to evaluate Smith's data, are ineffective in analysis of this particular type of

problem. Wilson,[20] prior to the availability of the data of Roellig and Giese, showed that the Redlich-Kwong equation, with modified temperature dependence of the 'a' parameter, predicted the temperature dependence of He solubility observed by Smith. Subsequent experimental data from the University of Michigan[10, 11, 13] provided the proof of Corruccini's conclusion and at least qualitative support of Wilson's calculations. Later, Staveley[21] noted that, even with the newer data, heats of solution derived from infinite dilution Henry's constants for the He^4 - H_2 system are less certain than for other low temperature systems he examined.

The objectives of the present investigation, established with due consideration of the above discussion, were to obtain a consistent set of liquid-vapor equilibrium data in the low pressure region for the He^4 - nD_2, He^3 - nD_2, He^4 - nH_2, and He^3 - nH_2 systems, and to provide a comparative reference with previous data. This investigation includes measurements on:

(a) the vapor pressures of nD_2 from 20 to 34 K and of nH_2 from 20 to 30 K;

(b) the compositions of the equilibrium liquid and vapor phases of the He^4 - nD_2 system from 20 to 30 K and the He^4 - nH_2 system from 20 to 28 K up to 20 atm (2 MN/m^2);

and

(c) the compositions of the liquid and vapor phases of the He^3 - nD_2 system from 20 to 30 K and the He^3 - nH_2 system (liquid phase only) from 22 to 28 K up to 16 atm (1.6 MN/m^2).

The maximum pressure was intentionally established below the barotropic locus of the He^4 - nH_2 system to avoid density instabilities, possible entrainment, and the necessity to reverse the direction of recirculation, as would be the case above the barotropic locus. The density inversion, which results when the molecular weight of the more volatile component is greater than that of the less volatile component, would thus occur at higher pressures for the He^3 - nH_2 system than for the He^4 - nH_2 system.

The pressures at which the densities of the two phases would be the same were estimated for the He^4 - nH_2, He^3 - nH_2, and He^4 - nD_2 systems, and were compared with the experimental observations for the He^4 - nH_2 system.[11] These are shown in figure 1. The barotropic locus for the He^4 - nD_2 system is of academic interest only since the actual density inversion may not appear below the locus of critical pressures. In these calculations, the density was assumed to be that of pure, saturated liquid; the molar volume of the vapor phase, calculated from the average molecular weight for the equilibrium vapor phase composition taken from Sneed et al.[11] and the corresponding liquid phase density,[22, 23] was assumed to be equivalent to the molar volume of pure He^4 [24] or He^3 [25] at the same temperature.

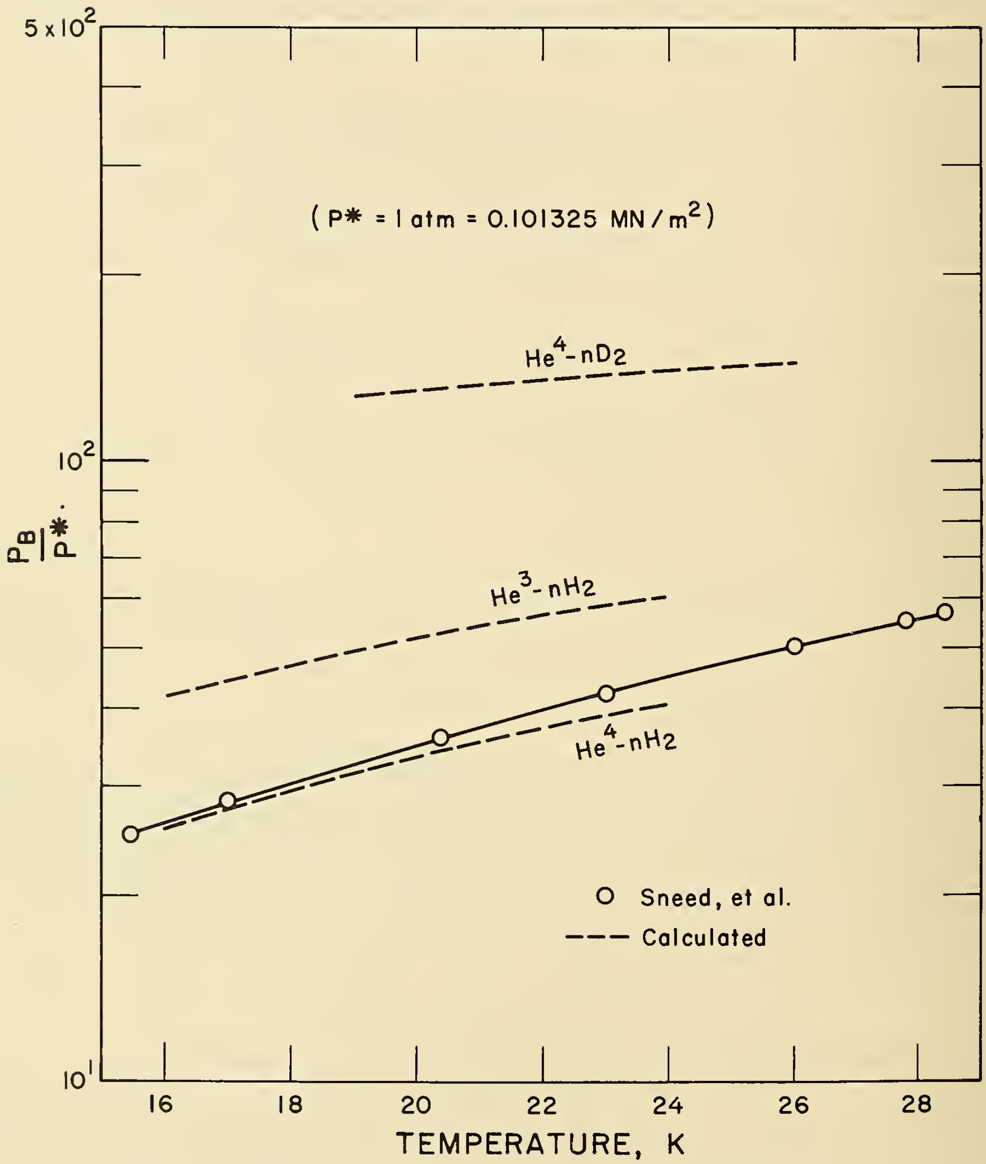

Figure 1. Estimated barotropic loci.

In contrast, for the He^4-nH_2 system at 20.4 K and at the same vapor phase composition used above, the barotropic pressure calculated from the mixutre virial equation of state, truncated after the second term, is significantly lower than that estimated above (approximately 25%). The interaction second virial coefficient of Knaap et al.[26] was used in determining the mixture second virial coefficient at the subject vapor phase composition. Since the second virial coefficient alone is inadequate to reproduce the pure He^4 properties[24] at this temperature and pressure, it appears that the mixture third virial coefficient, which is usually not available, is required for this calculation.

2. Experimental Method

The apparatus used in these measurements is a modified design of the apparatus of Duncan and Hiza[27] with the same type of pump[28] for recirculation of the vapor. A schematic flow diagram of the apparatus is shown in figure 2, and the arrangement of the components within the cryostat is shown in figure 3.

The equilibrium cell, made of electrolytic tough pitch copper, has an internal volume of 19.8 cm^3, an internal diameter of 2.48 cm, and an outside diameter of 6.35 cm. The closure is a threaded copper plug soft-soldered in place; a double layer of fine mesh screen covers the equilibrium vapor exit in the center of the plug to serve as an entrainment separator. The platinum resistance thermometer (PRT) well extends from the top of the cell to a point approximately one-third of the distance from the bottom of the equilibrium cavity. Thus, differential temperature measurements from the top of the cell to the bottom of the equilibrium cavity were not considered necessary. The PRT, calibrated on the IPTS-68 Kelvin scale, is secured in place with Wood's metal.

The temperature of the equilibrium cell is controlled by balancing refrigeration provided by cold hydrogen vapor from the refrigerant reservoir (of 2.25 l capacity) with an automatically regulated 120 ohm heater, noninductively wound on the cell just below the equilibrium cavity. The heater power regulator is a transistorized unit designed by Jellison.[29] The desired temperature is obtained by controlling the voltage drop across the PRT; the unbalance from the selected voltage drop, as sensed by a potentiometer, is amplified with a breaker amplifier and fed to the power regulator for heater control. With this arrangement, the experimental temperature could be maintained, generally within ± 0.005 K, for any desired length of time. The maximum uncertainty in temperature is thought to be ± 0.01 K.

The cell pressure was measured with a 300 psia, double-revolution, Bourdon tube gauge. Though the smallest scale division of this gauge is 0.5 psia (equivalent to 0.034 atm), a finely divided machinist rule was used to estimate lower subdivisions to approximately ± 0.05 psia. The maximum uncertainty of the gauge is claimed to be

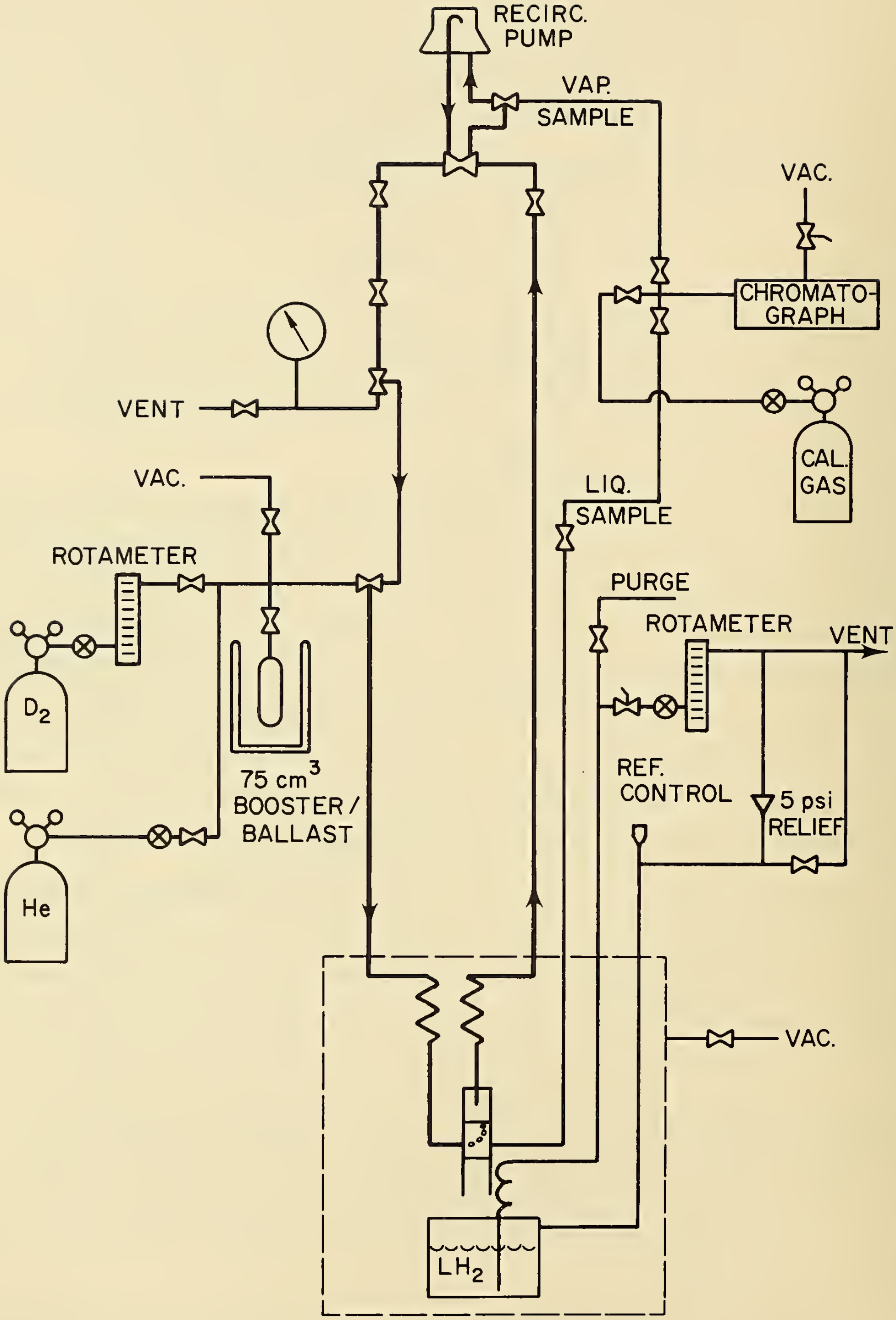

Figure 2. Schematic diagram of the experimental apparatus.

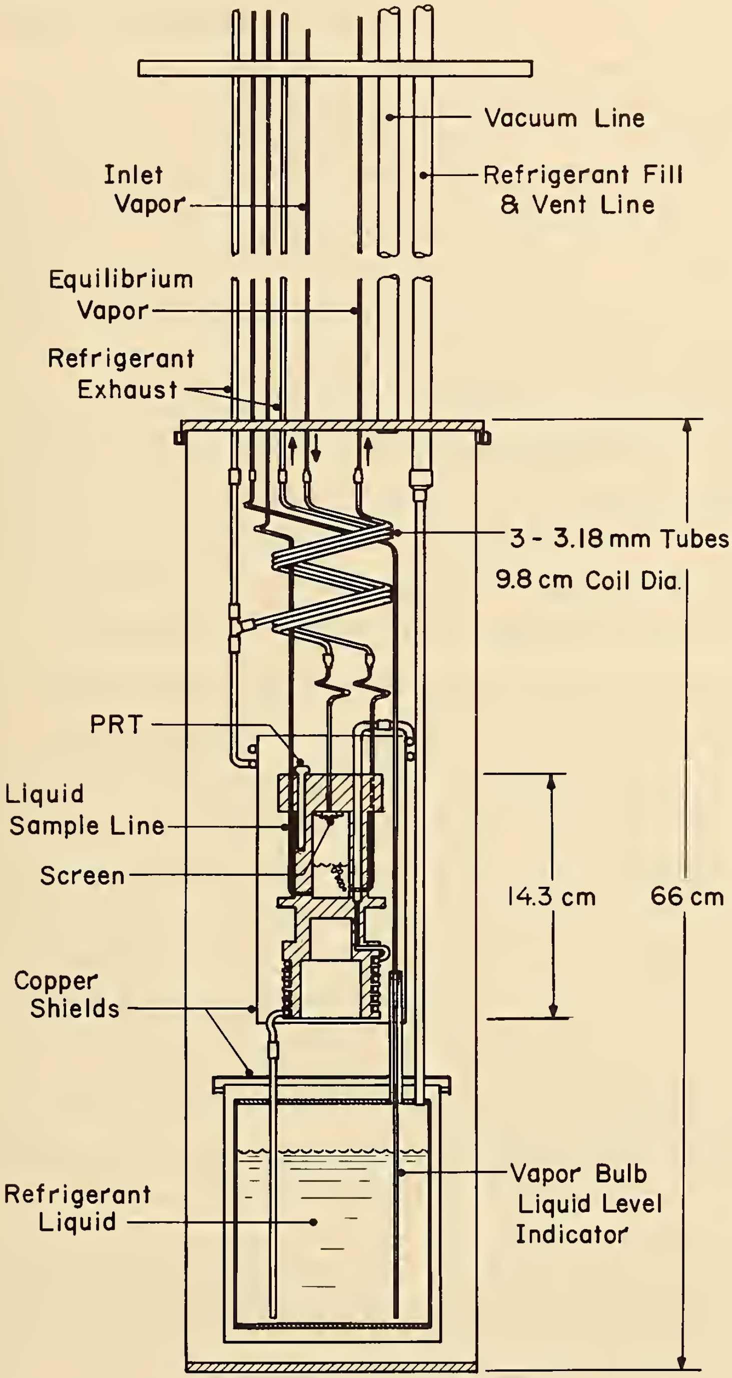

Figure 3. Details of the equilibrium cryostat.

$\pm$ 0.1% of full scale and repeatability within $\pm$ 0.066% of full scale. The gauge was set at atmospheric pressure with a barometer reading corrected for temperature and gravity. Gauge readings were then checked against a laboratory dead-weight gauge and were found to meet the accuracy claims of the manufacturer. At 50 psia no difference in readings could be detected; at 150 psia the Bourdon tube gauge reading was 0.065% low; and at 300 psia the Bourdon tube gauge reading was 0.089% low.

All fluids introduced into the equilibrium cell were purified with a small, liquid nitrogen cooled, silica gel adsorber (not shown in figure 2) on the feed cylinder side of the booster volume. Thus, only the level of impurities of He or H_2 isotopes or Ne in the feed gas are of significance. The He^4 was standard U.S. Bureau of Mines Grade-A He, and the H_2 was purified gas obtained from the NBS liquid and gas distribution facility. Since the H_2 cylinders are often filled with boil-off gas, a cylinder which had been filled several months prior to use was selected so that normalization would not be required. Thus, He^3 and higher hydrogen isotopes would be present in the He^4 and H_2 in natural abundance. The He^3 and D_2 and the analyses were supplied by the U.S.A.E.C. The He^3 contained 1.4 mole % He^4, and the D_2 contained 1.12 mole % HD and 0.02 mole % H_2. These isotopic impurity levels in the He^3 and D_2 gas were not expected to produce detectable differences in the phase equilibrium properties measured here.

Compositions of the equilibrium phases were analyzed by gas chromatography with thermistor detectors. To avoid the well known peak-folding phenomenon, due to thermal conductivity reversal of He - H_2 mixtures,[30] the mixtures were separated with an 11.9 meter column of 3.18 mm I.D. tubing packed with 80 mesh molecular sieves 5A. Ar was used as the carrier gas at 50 to 55 cm^3/min flowrate. Pressure drop through the column was approximately 1.3 atm (0.13 MN/m^2). Samples were injected at various pressures, generally between 0.6 and 0.8 atm (0.06 and 0.08 MN/m^2, respectively), using a 0.3 cm^3 sample loop on the injection valve. With this arrangement, the time lapse between injection and the start of the He and H_2 peaks was approximately 15 and 23 min, respectively.

Equilibrium liquid phase samples were withdrawn directly from the bottom of the cell through a 0.178 mm I.D. stainless steel capillary tube. This capillary tube is joined to a tube of 1.19 mm I.D., also of stainless steel, about 15 cm above the top of the cell. The internal volume of the larger tube is filled with a copper wire, of slightly smaller diameter, approximately 50 cm in length. Equilibrium vapor phase samples were withdrawn from the recirculation pump cavity, which was isolated with inlet bypassed to the outlet during sampling. In both cases, the recirculation pump was turned off during sampling. Due to the excessive analysis time (approximately 30 to 35 min) and to the

large differences in compositions of the two phases, it was more convenient to determine liquid and vapor phase compositions in separate runs. A vapor pressure check at the beginning of each run was used to confirm the reproducibility of experimental conditions. These vapor pressure measurements were made in both static and recirculation modes with no detectable difference in results.

The chromatograph was calibrated for liquid phase measurements with a mixture of 5.27 mole % He^4 in Ar. This mixture was prepared on a partial pressure basis, assuming ideality, at a total pressure of 18 atm (1.8 MN/m^2). The use of Ar as the second component in the mixture in lieu of nH_2, for example, eliminates the second peak, thus significantly reducing the time required for calibration. However, a second mixture of 10.00 mole % He^4 in nH_2 was prepared, also assuming ideality at a total pressure of 15 atm (1.5 MN/m^2), to verify the primary reference mixture and to ensure that separation was adequate to avoid interference between a large nH_2 peak and a relatively small He^4 peak. An estimate of the nonideality of each mixture indicated that the actual compositions were 5.22 mole % He^4 in Ar and 10.08 mole % He^4 in nH_2. Interaction second virial coefficients from Brewer and Vaughn[31] with selected values of the second virial coefficients for He^4,[24] Ar,[32] and nH_2[33] were used in these estimates. The relative magnitude of the difference between the ideal and corrected compositions was approximated in the comparative analyses. Since the uncertainty was no more than 1%, the ideal composition of the He^4-Ar reference was used as the basis of all liquid phase analyses.

The chromatograph was calibrated for vapor phase measurements with mixtures of 50.00 mole % He^4 in nD_2, prepared at 6 atm (0.6 MN/m^2), and 50.00 mole % He^4 in nH_2, prepared at 9.5 atm (0.95 MN/m^2), also using the ideal mixture compositions. Comparative analyses of these mixtures were in agreement within less than 1% of the He^4 content. Comparison of the nD_2 and nH_2 content with pure nD_2 and nH_2, respectively, at the same partial pressure verified this agreement.

For He^3 analysis, the peak area was adjusted to the equivalent He^4 response for comparison with the appropriate standard. The ratio of integrated peak areas of $He^4:He^3$, for indentical samples of the pure species, was found to be 0.858 by repetitive chromatographic analyses.

The uncertainty in the compositions of the equilibrium liquid and vapor phases is thought to be ± 3% of the reported concentration of the minor component, or ± 0.1 mole %, whichever is greater.

3. Experimental Results

A. Vapor Pressure of nD_2 and nH_2.

Though vapor pressure measurements were intended only as verification of the experimental technique, discrepancies in published vapor pressure values for nD_2 made a more detailed study of this property desirable. Measurements made generally at one K increments for nD_2 from 20 to 34 K and for nH_2 from 20 to 30 K, were fitted to an Antoine equation of the form

$$\ln p_o(\mathrm{atm}) = A - B/(T + C) \tag{1}$$

This simple form allows convenient interpolation and evaluation of the normal boiling point temperature of each isotope. At the normal boiling point, equation (1) reduces to

$$T_{nbp} = (B - AC)/A \tag{2}$$

The constants of equation (1) and vapor pressure values are given in table 1 for nD_2 and in table 2 for nH_2.

The normal boiling point of nD_2 listed by Woolley, Scott, and Brickwedde[34] is almost exactly 0.1 K lower than the value found in this investigation. The vapor pressure of nD_2, upon which the equation of Woolley et al. is based, was measured[35] relative to the vapor pressure of nH_2 only up to 20.4 K. Thus, the normal boiling point of nD_2 reported was found by extrapolation. Subsequent measurements on uncatalyzed D_2 reported by Hoge and Arnold[36] and Grilly[37] give normal boiling points of 23.666 K and 23.665 K, respectively. Deviations of the four sets of nD_2 vapor pressure values are shown in figure 4 relative to equation (1) fitted to the present data. The larger deviations at the low temperature end result from weighting the data for uncertainty in pressure measurement during curve fitting. The remarkable agreement of the normal boiling point (23.666 K) obtained from the fit of the present data with those resulting from the measurements of Hoge and Arnold and of Grilly is somewhat fortuitous, since the fit of the data is obviously not that good and the apparatus used in this investigation was not specifically designed for precise vapor pressure measurement.

Whereas the low temperature portion of the present nD_2 vapor pressure measurements tend to reflect the lack of precision of pressure measurement, the present nH_2 vapor pressure measurements are generally more indicative of the precision of temperature measurement in the range of investigation. The normal boiling point of nH_2 reported by Woolley et al. is 0.014 K higher than that found from this investigation. Grilly[37] and Van Itterbeek et al.[38] also report vapor pressure data for nH_2 in the region of interest. Deviations of these sets of nH_2 vapor pressure values are shown in figure 5 relative to equation (1) fitted to the present data.

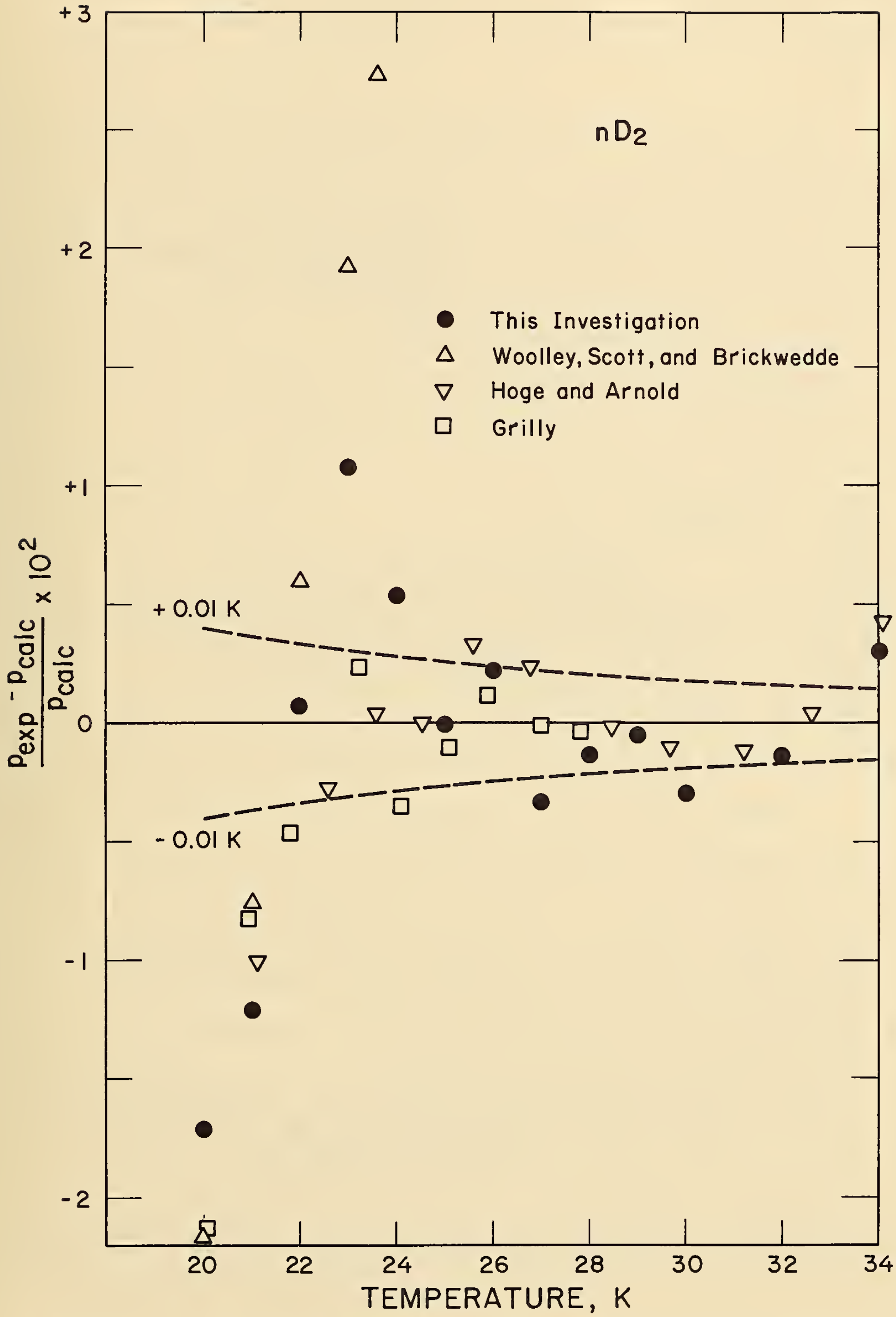

Figure 4. Deviations of vapor pressure data for nD_2 from equation 1.

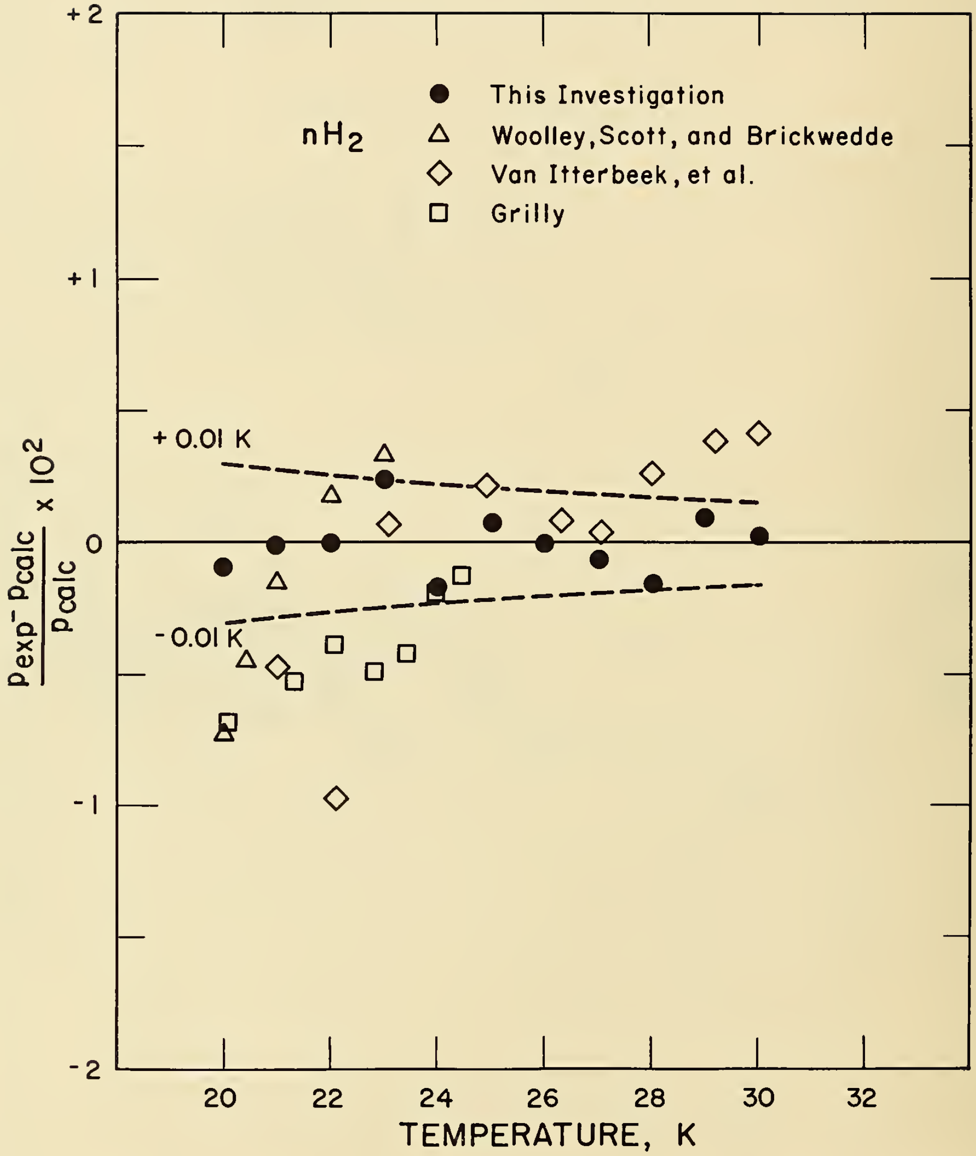

Figure 5. Deviations of vapor pressure data for nH_2 from equation 1.

The agreement of the present vapor pressure measurements for nD_2 and nH_2 with other measurements for these fluids is considered adequate for present purposes. The only significant discrepancy, i.e. with the nD_2 vapor pressure values of Wooley et. al. above 21 K, clearly is the result of error in the extrapolation of Wooley et al based on rather limited data.

B. Solubility of He^4 and He^3 in Liquid nD_2 and Liquid nH_2.

Results of the measurements on the equilibrium liquid phase compositions of the He^4 - nD_2, He^3 - nD_2, He^4 - nH_2, and He^3 - nH_2 systems are given in tables 3 - 6. These results are plotted in figures 6 - 9 as mole % of He^4 or He^3 as a function of the total system pressure minus the vapor pressure of the liquid solvent, which is roughly equivalent to the He partial pressure. The actual He partial pressure would be given by the product of the total pressure and the mole fraction of He in the equilibrium vapor. At each temperature, $P - p_{o1}$ was determined using the experimental vapor pressure. The form of representation used in figures 6 - 9 avoids crossing of the isotherms but retains the original curvature of the composition versus total system pressure isotherms.

In all four systems, the solubility of He^4 or He^3 increases with increasing temperature at constant He partial pressure. At the same temperature and partial pressure, the solubility of He^4 or He^3 in liquid nH_2 is approximately twice as large as that in liquid nD_2. In addition, the solubility of He^4 is approximately 10 - 20% larger than the solubility of He^3 in either solvent. It should be noted that the 26 K isotherm for nH_2 systems is approximately at the same reduced temperature (of the solvent) as the 30 K isotherm for the nD_2 systems. Even then, the solubility in nH_2 is still somewhat larger.

Solubility data also are often represented as Henry's law diagrams. These normally consist of the ratio of the fugacity of the solute in the vapor to its mole fraction in the liquid plotted as a function of the solute fugacity in the vapor. For the systems and conditions under consideration, the solute fugacity is not greatly different than the solute pressure. Thus, the Henry's law diagrams for the liquid phase data of this investigation, as given in figures 10 - 13, are based on pressure. The dashed curves represent isotherms determined by extrapolation. These diagrams more clearly expose experimental discrepancies and are a valuable aid in smoothing the liquid phase data.

The intercepts of the curves at zero solute fugacity are also of great interest in correlation attempts and theoretical analysis. The intercepts are commonly referred to as the infinite dilution Henry's constants, that is

$$\lim_{f_2 \to 0} (f_2/x_2) = H_2^{\infty} \qquad (3).$$

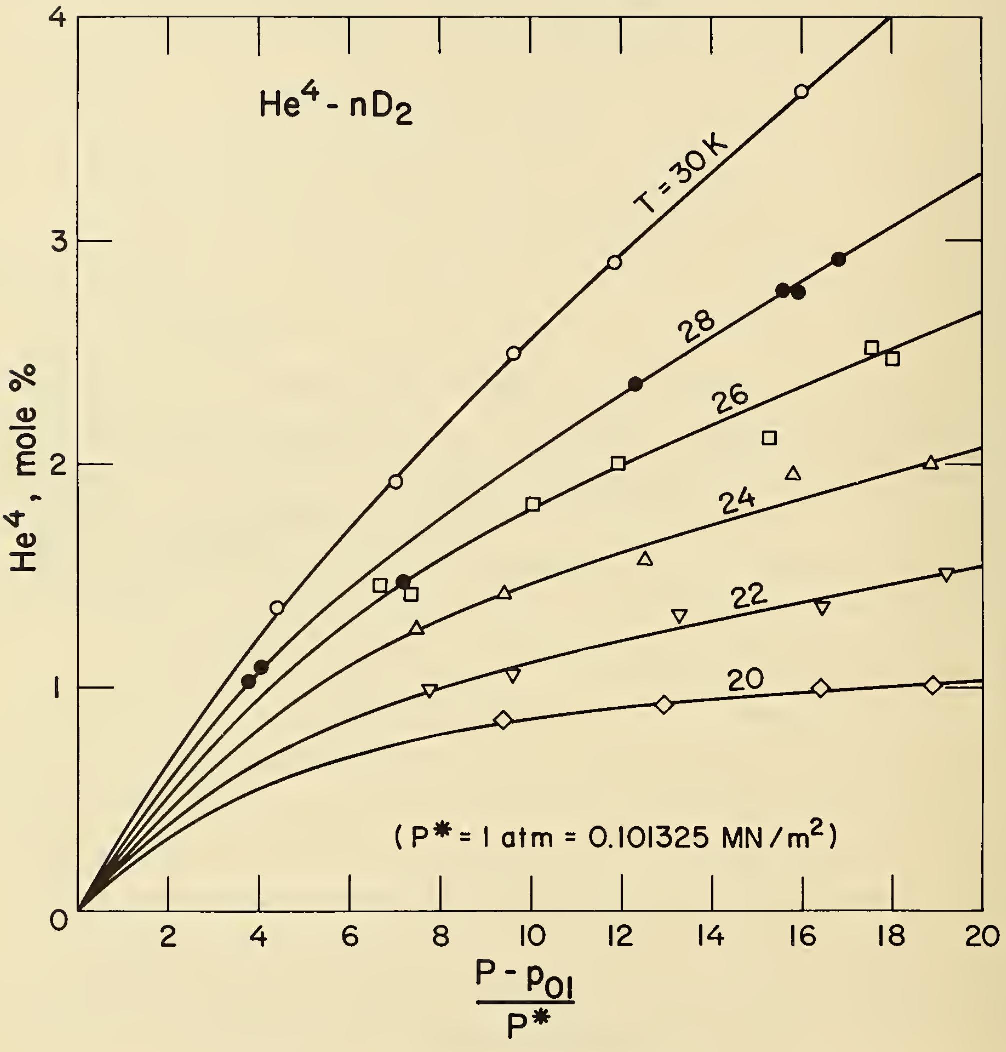

Figure 6. Solubility of He^4 in liquid nD_2.

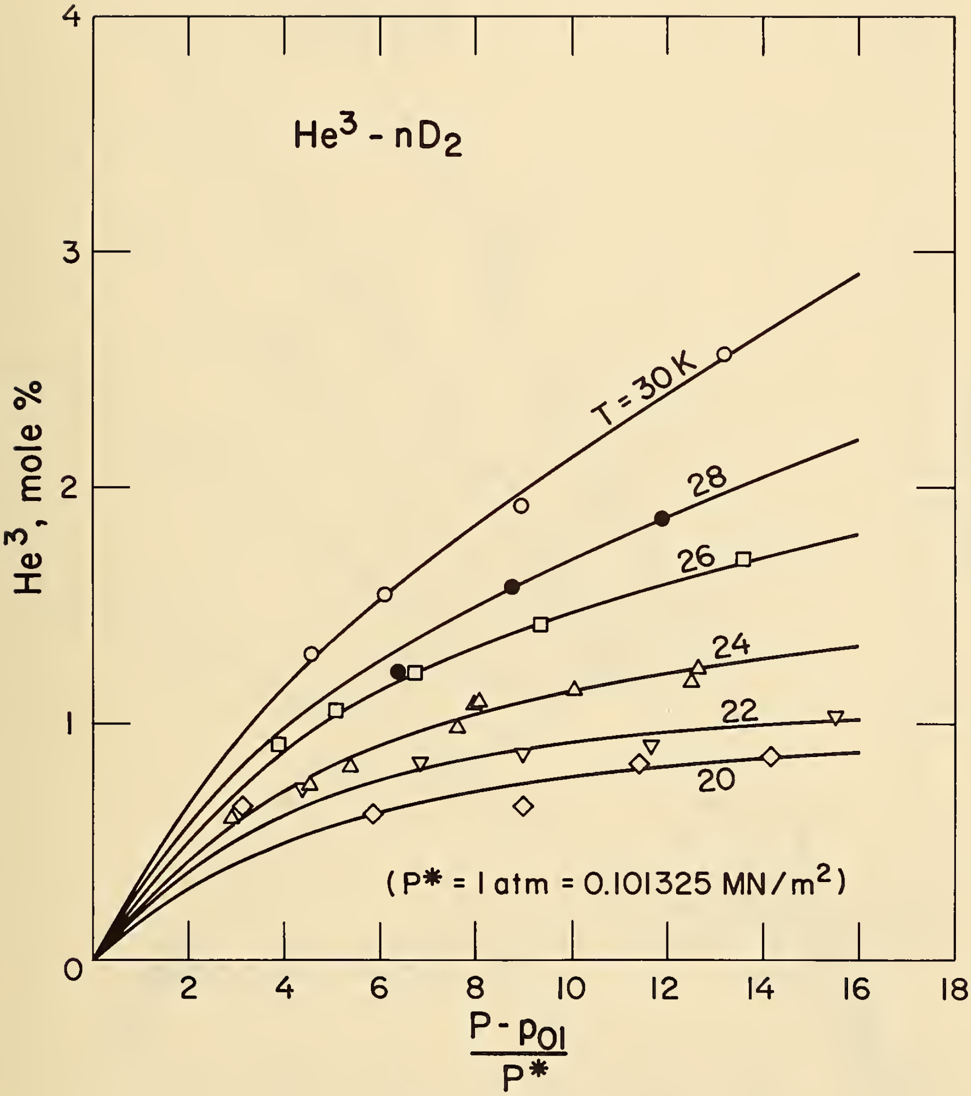

Figure 7. Solubility of He^3 in liquid nD$_2$.

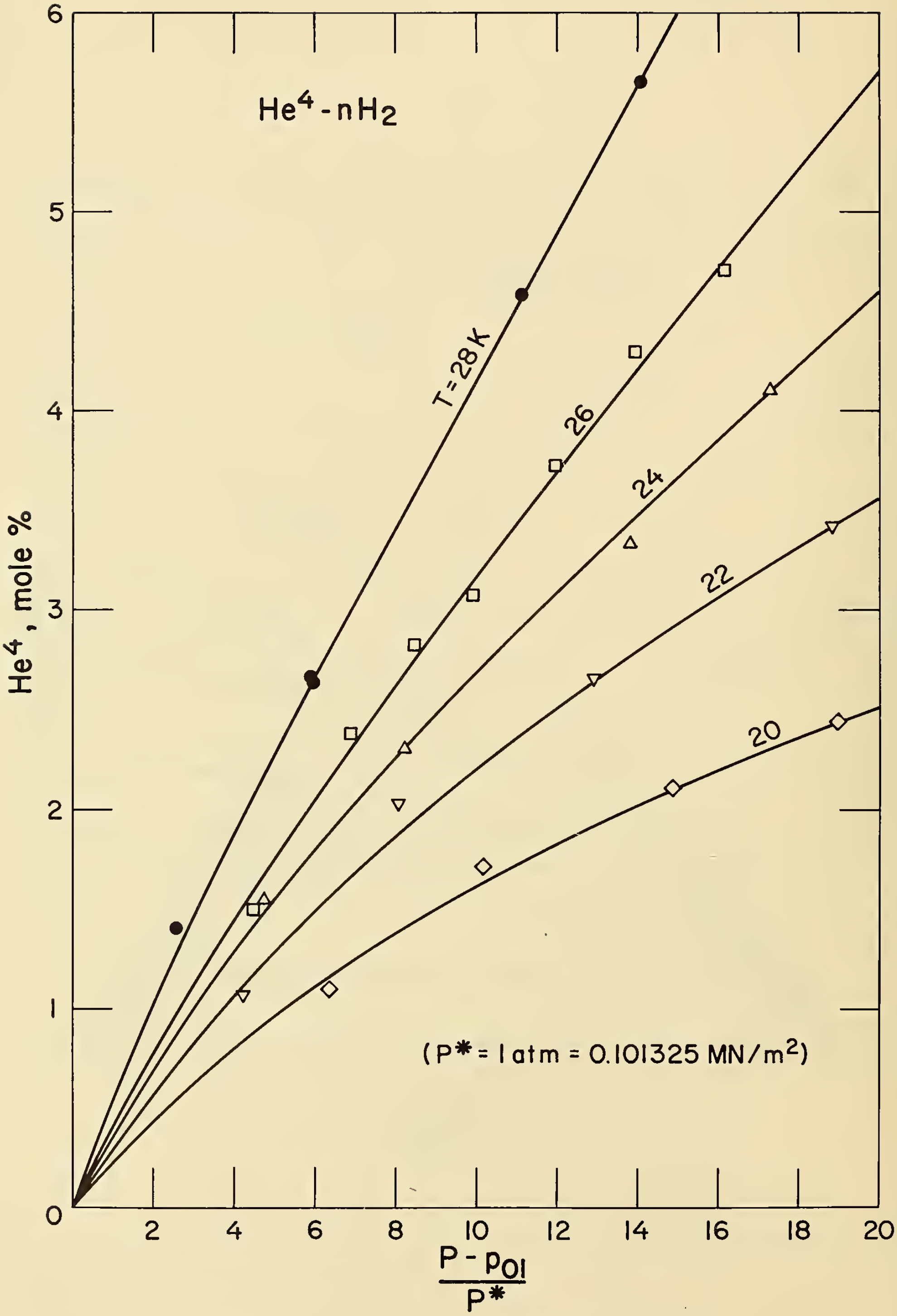

Figure 8. Solubility of He^4 in liquid nH_2.

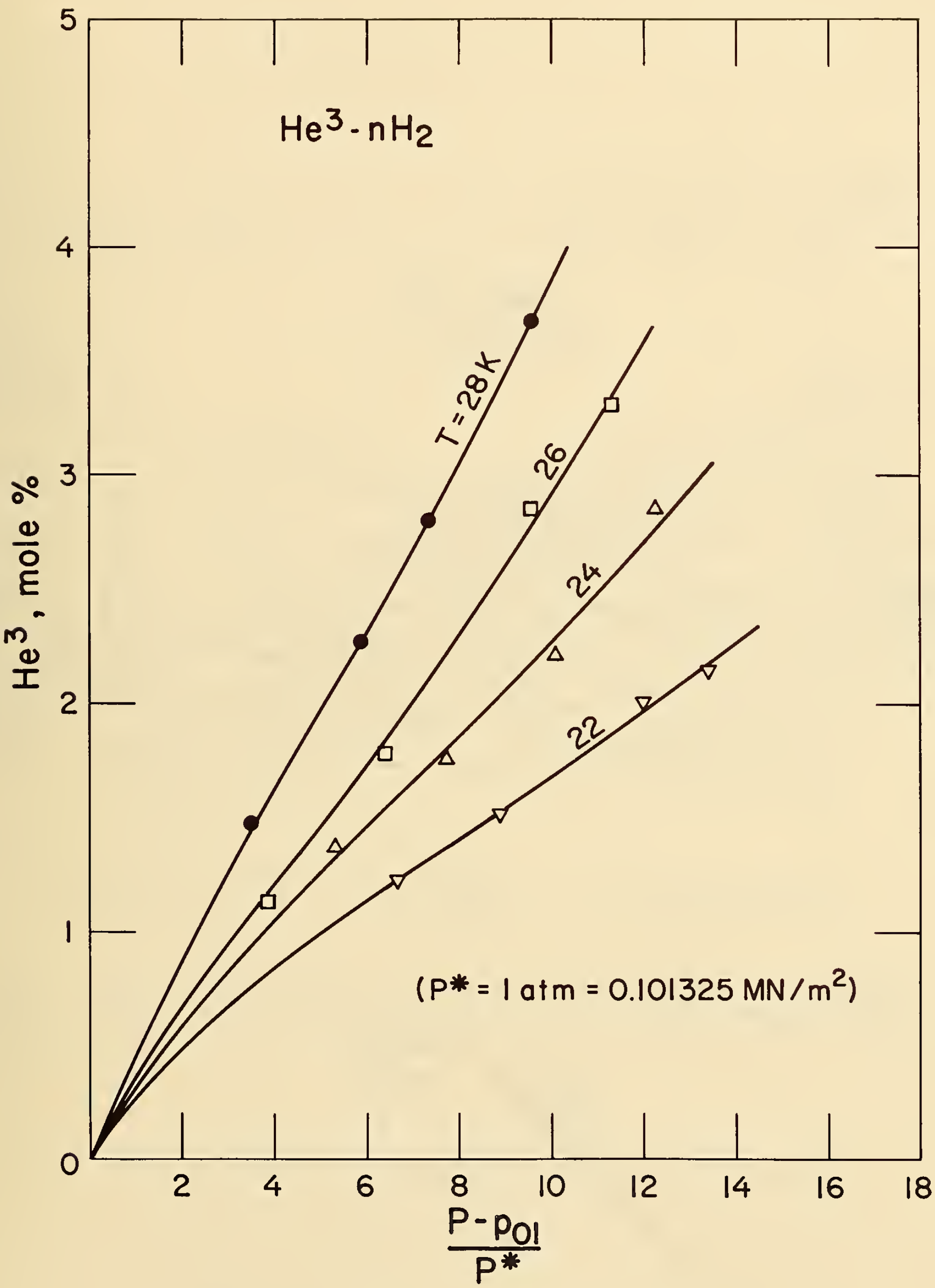

Figure 9. Solubility of He^3 in liquid nH_2.

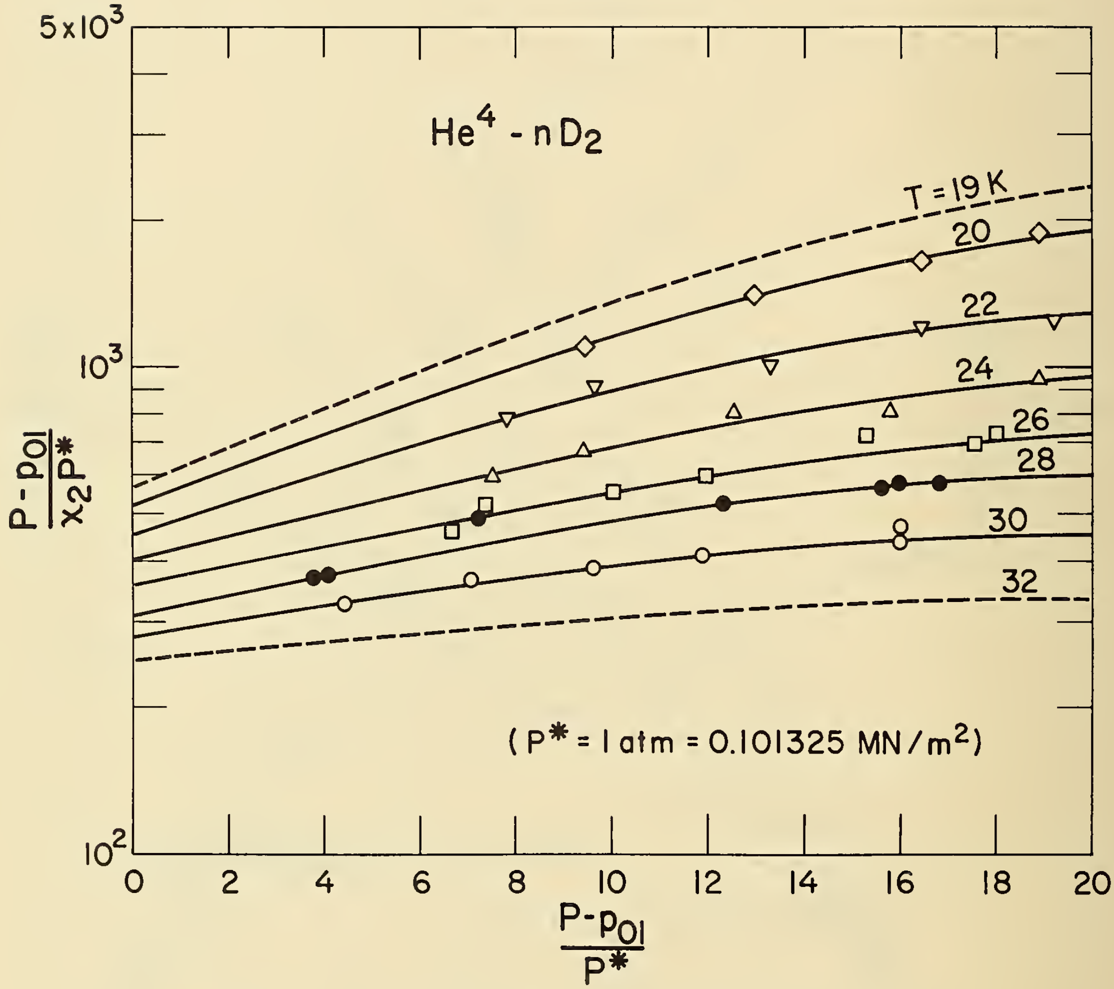

Figure 10. Henry's law values for He^4 in liquid nD_2.

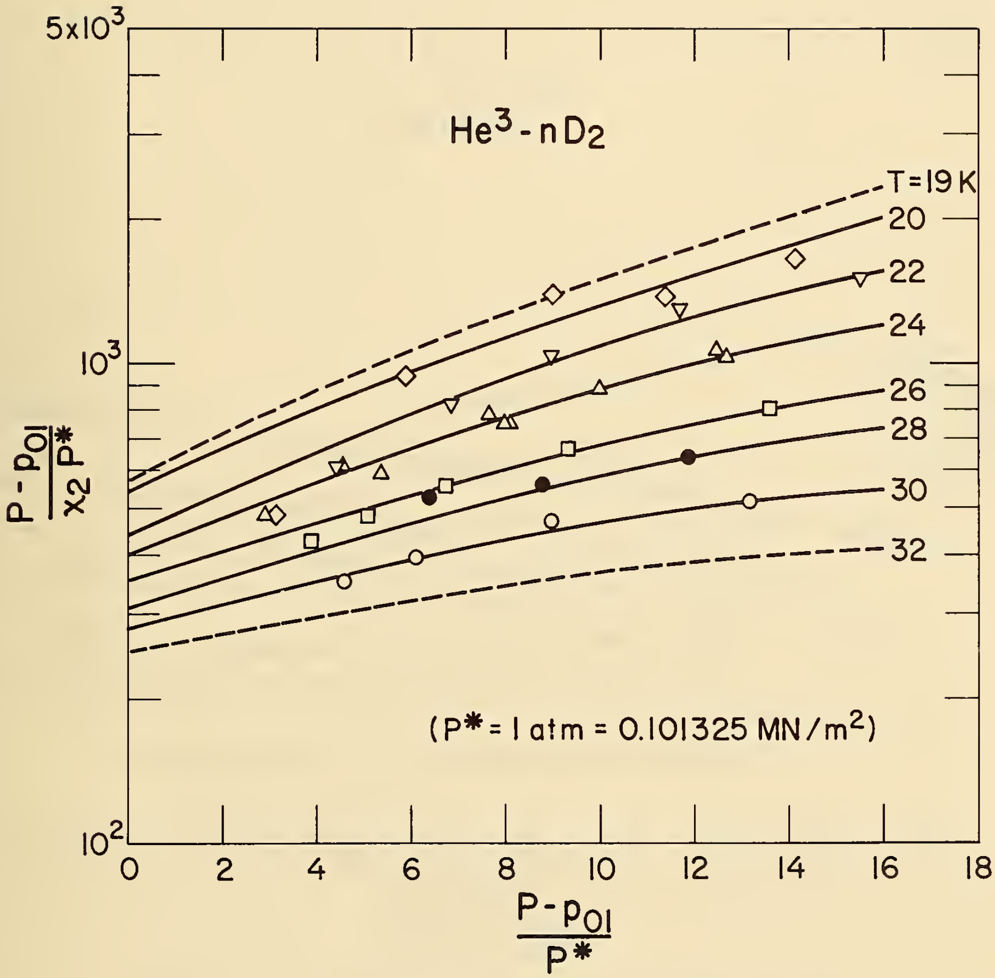

Figure 11. Henry's law values for He^3 in liquid nD_2.

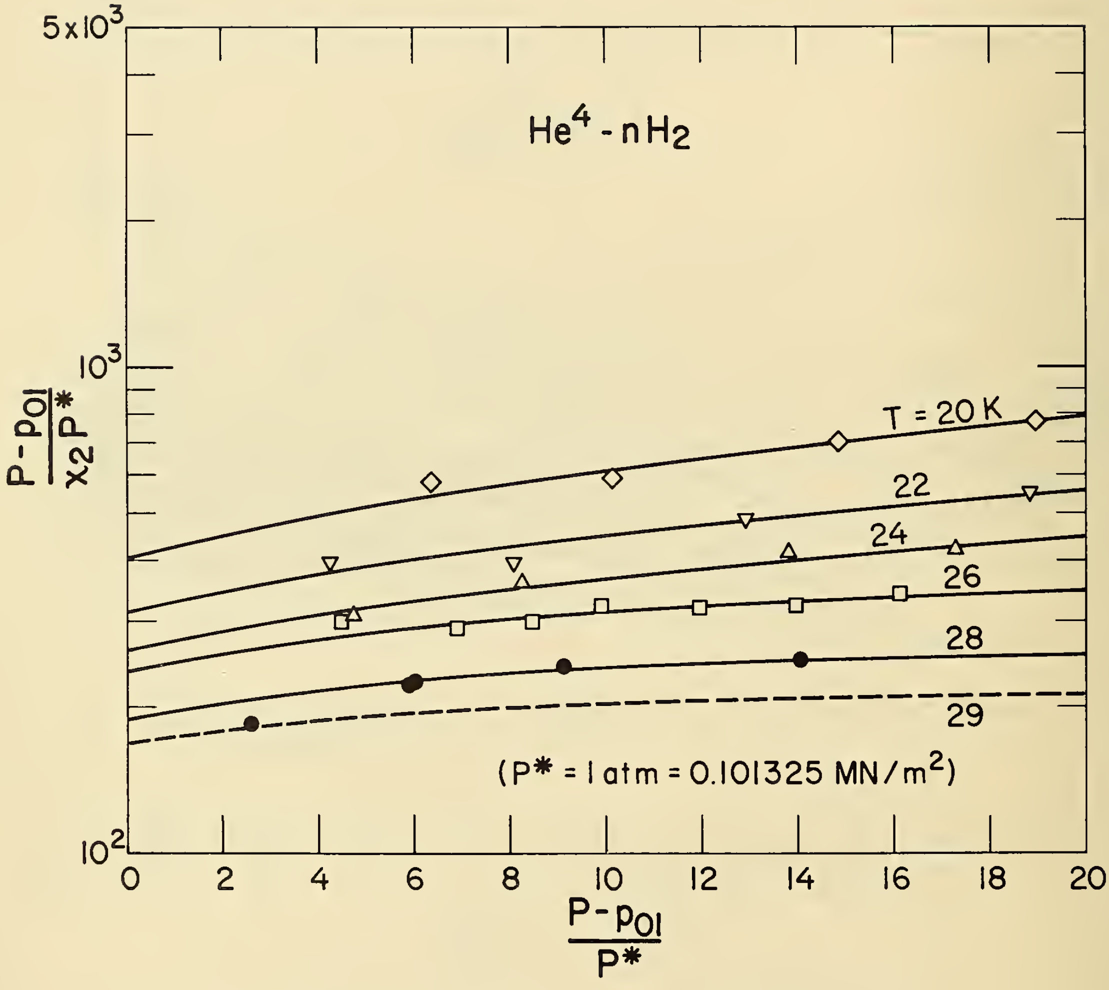

Figure 12. Henry's law values for He^4 in liquid nH_2.

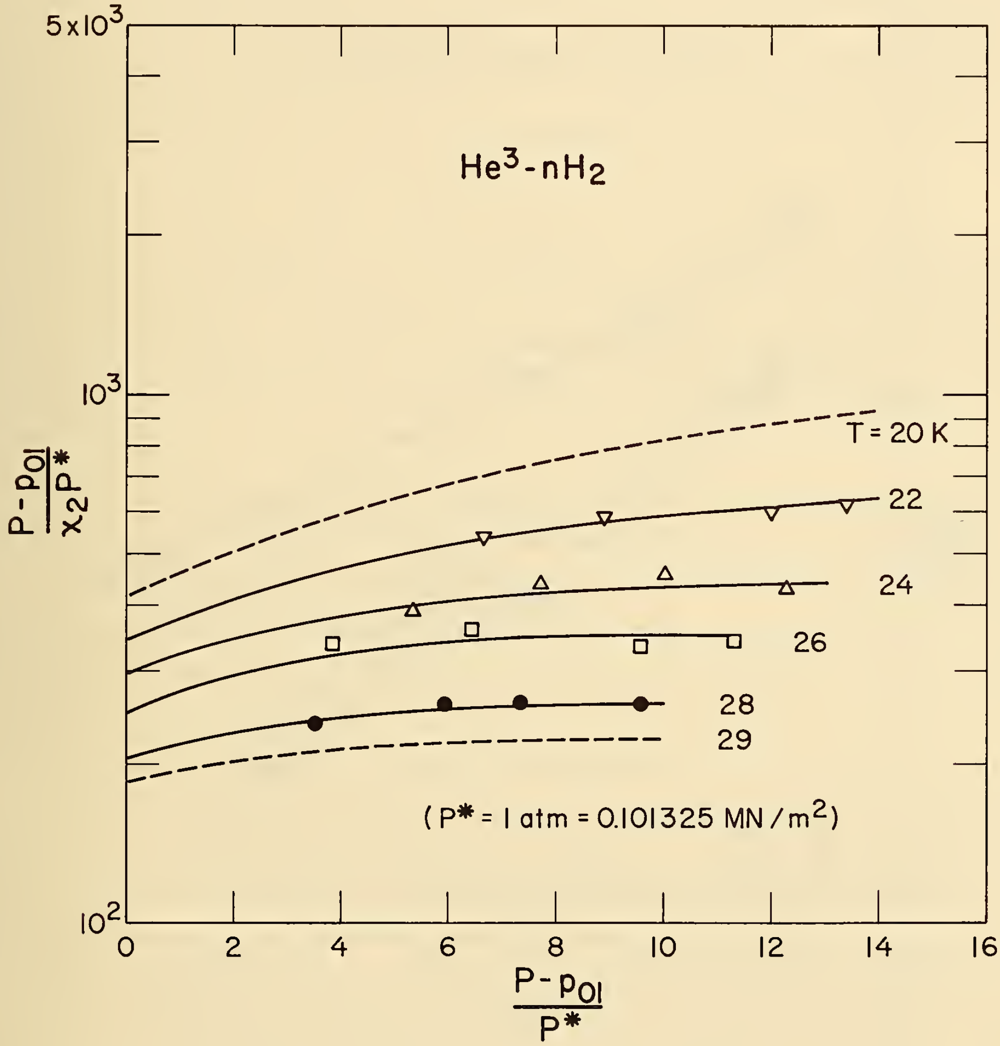

Figure 13. Henry's law values for He^3 in liquid nH_2.

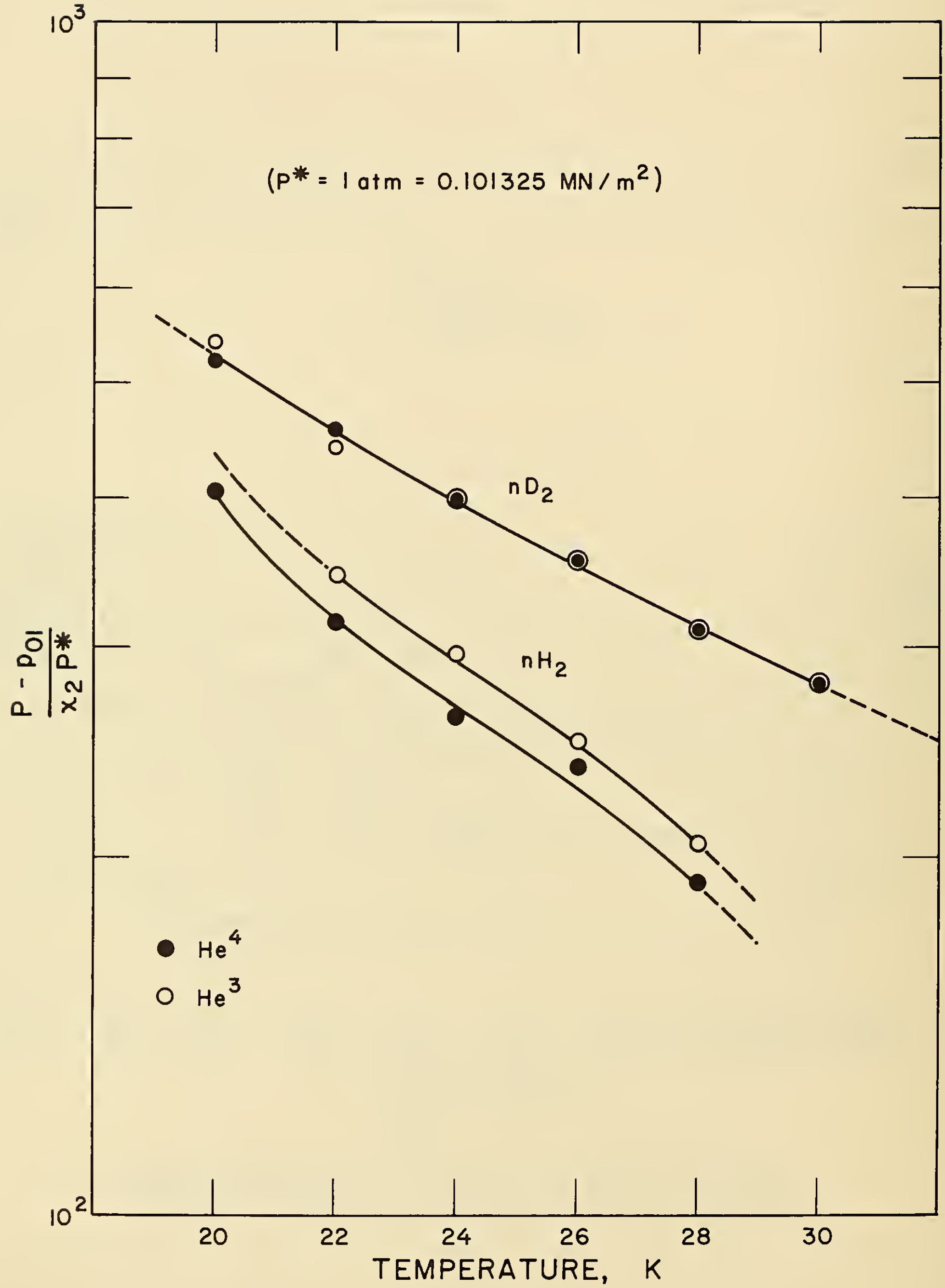

Figure 14. Infinite dilution Henry's constants.

The difficulty of obtaining infinite dilution Henry's constants is quite obvious; the necessary extrapolation is strongly affected by the degree of nonlinearity of the curves, the precision of the data, and any systematic errors. Infinite dilution values were obtained for the four systems studied here using both the curves in figures 6 - 9 and those in figures 10 - 13. The results, shown in figure 14, reflect the fact that the solubility of He is significantly greater in nH_2 than in nD_2 and the fact that He^4 is slightly more soluble than He^3. It should also be noted that the infinite dilution Henry's constants for the two He isotopes are also somewhat lower for the nH_2 systems at 26 K than the corresponding values for the nD_2 systems at 30 K. The fact that He^4 and He^3 have identical values with nD_2, rather than reflecting the slight difference in solubility as with nH_2, is related to the difficulty of the extrapolation and is not considered significant.

C. Vapor Phase Saturation Limits of nD_2 and nH_2 in He^4 and He^3.

Results of the measurements on the equilibrium vapor phase compositions of the He^4-nD_2, He^3-nD_2, and He^4-nH_2 systems are given in tables 7 - 9. Measurements were not made for the He^3-nH_2 system when no significant difference was found in the vapor phase compositions between the He^4-nD_2 and He^3-nD_2 systems within the pressure limits of the measurements.

The vapor phase data are best evaluated by examination of enhancement factors, i.e., the ratio of partial pressures of the condensible component to its normal vapor pressure at the same temperature. Enhancement factors are a direct indication of the non-ideality of the vapor phase, and at least in the low pressure region (removed from the critical region of the condensible component) can be represented by a rigorous theoretical model.[1]

Enhancement factors for both the He^4-nD_2 and He^3-nD_2 systems are shown in figure 15. Within the pressure and temperature limits of this investigation, no significant difference is indicated in the vapor phase properties due to the isotopic differences of He^4 and He^3. This is not entirely surprising when a comparison of enhancement factors is made for systems such as H_2-Ar[39] and Ne-Ar,[40] near the normal boiling point of Ar, up to 10 atm (1 MN/m^2) or so. Even though the major components interact quite differently with the common condensible component, Ar, the difference reflected in the enhancement factors only becomes apparent as the pressure is advanced.

The enhancement factor curves for the He^4-nD_2 and He^3-nD_2 systems are cross-plotted in figure 16 at constant system pressure. A property of the enhancement factor, which should be apparent in figures 15 and 16, is that its value must approach unity as the system pressure approaches the vapor pressure of the condensible component. As defined here, enhancement factors less than unity have not been observed (outside the

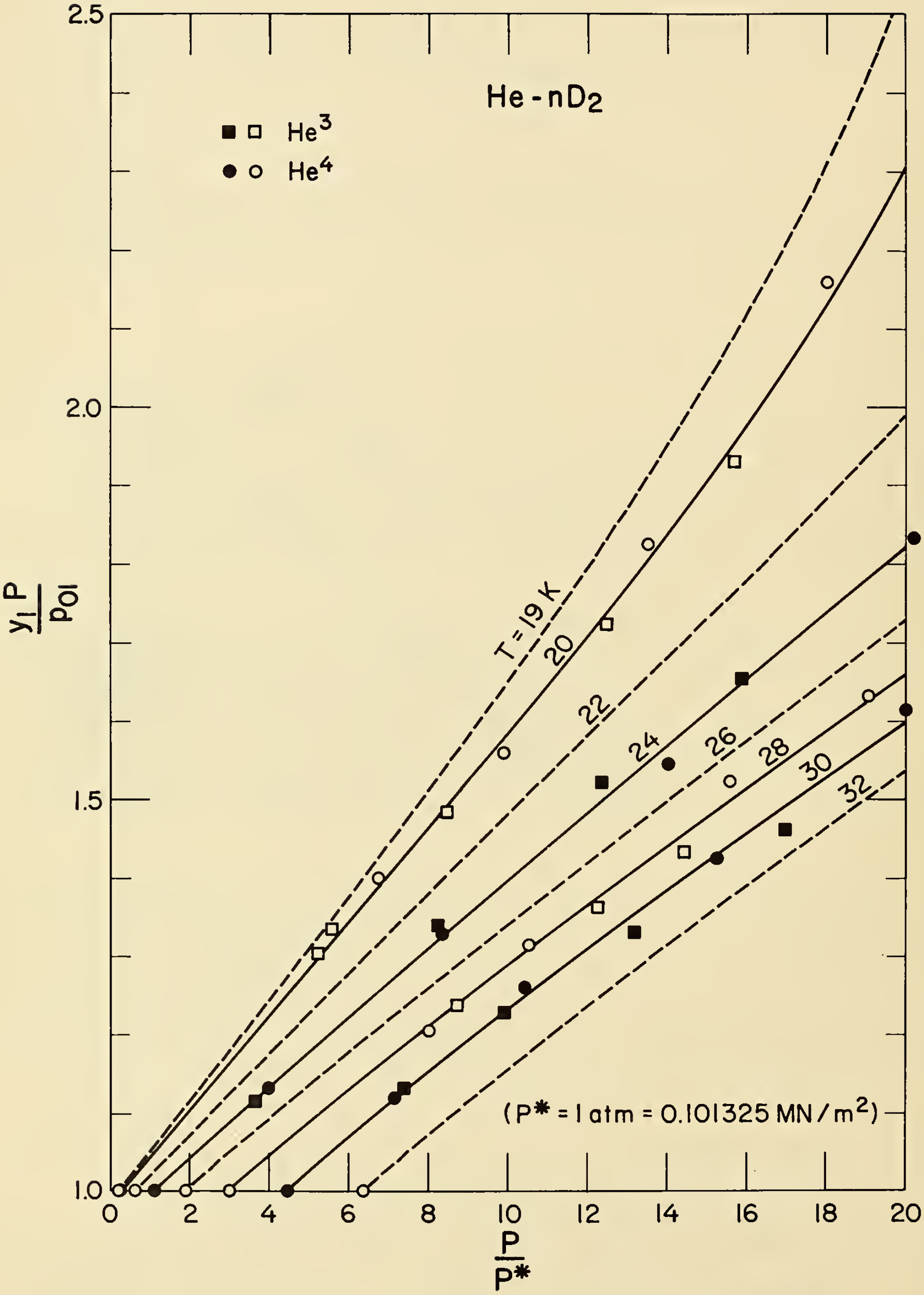

Figure 15. Isothermal enhancement factors for the He^4-nD_2 and He^3-nD_2 systems.

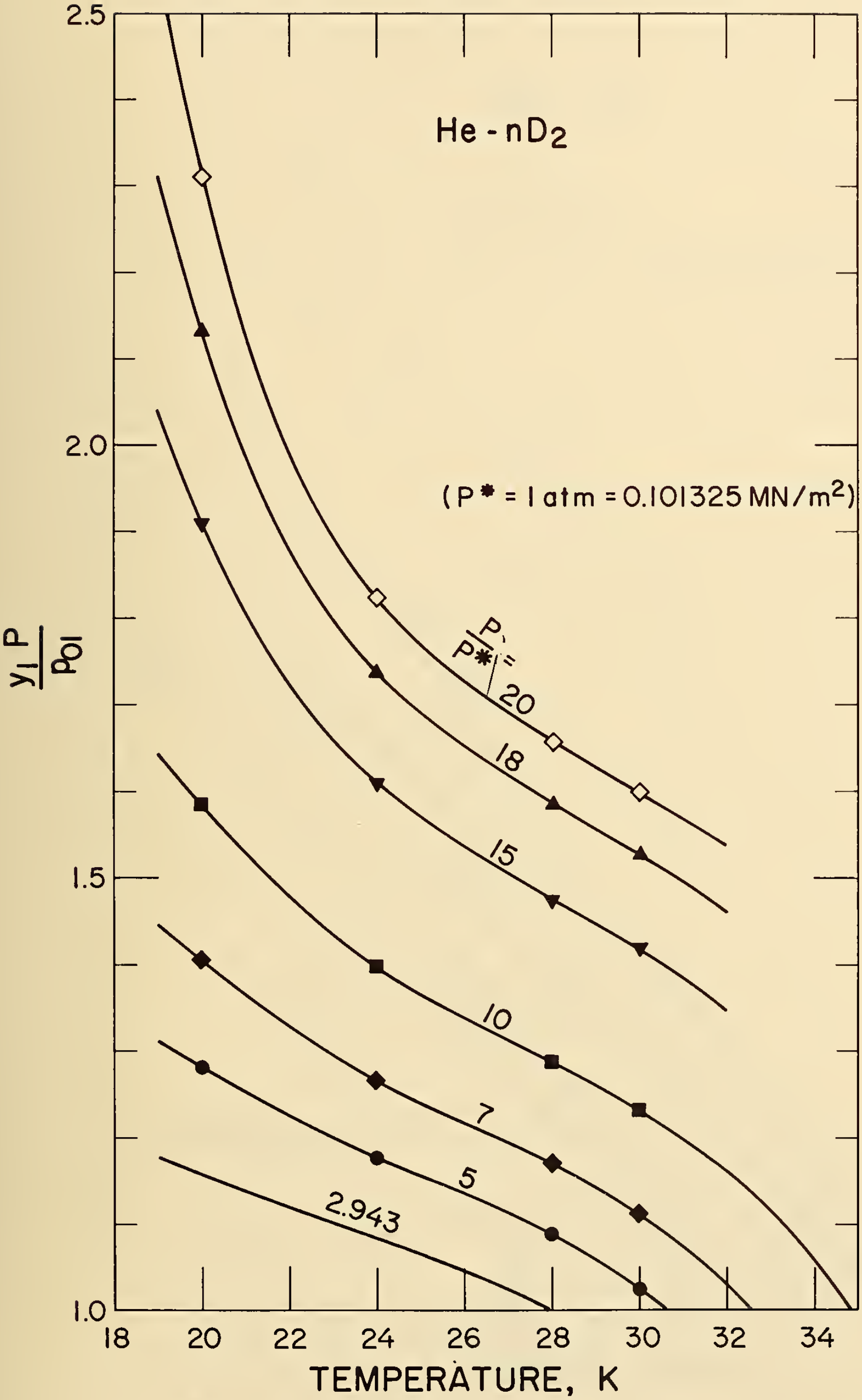

Figure 16. Enhancement factors for the He^4-nD_2 and He^3-nD_2 systems at constant system pressure.

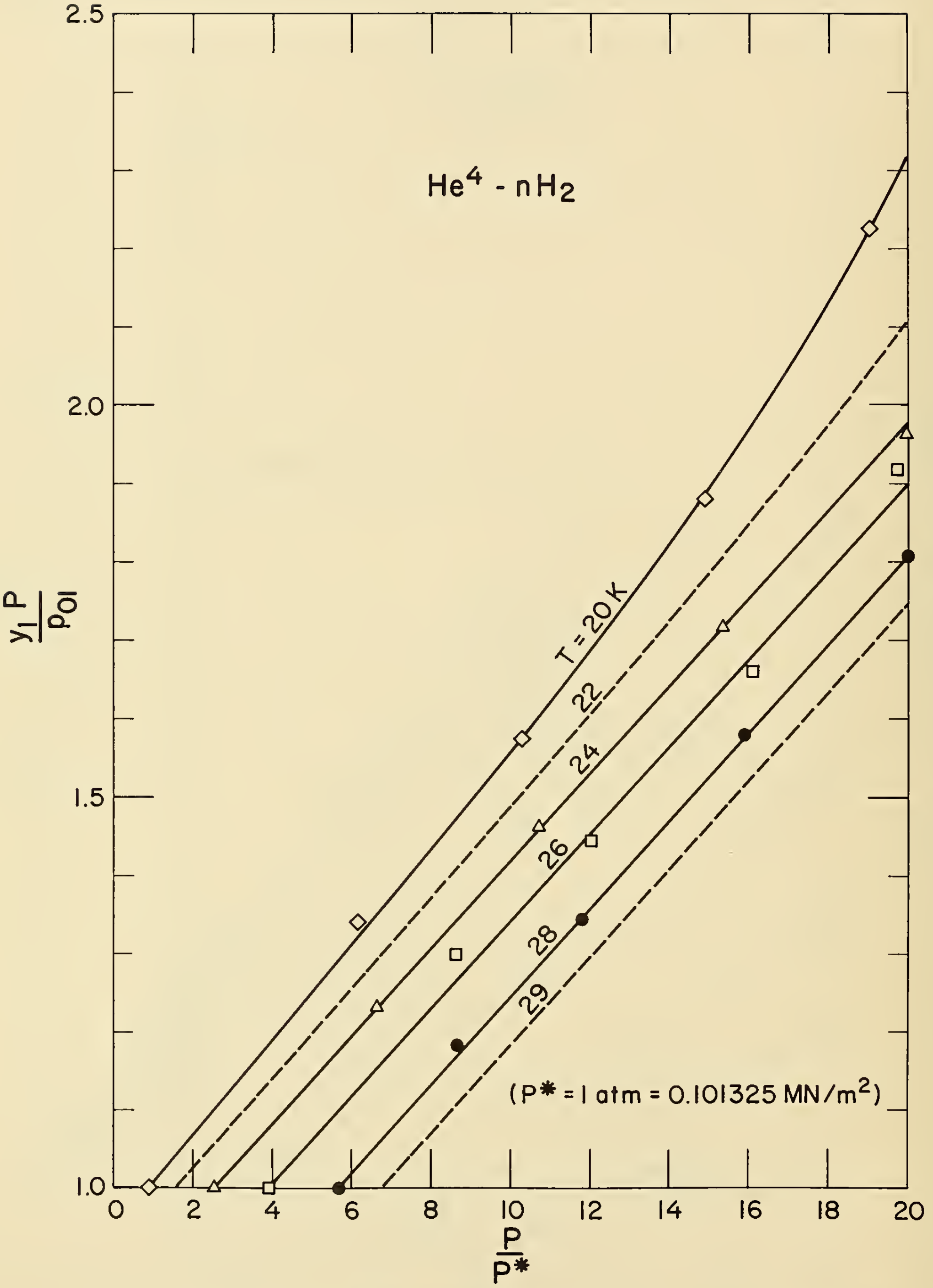

Figure 17. Isothermal enhancement factors for the He^4-nH_2 system.

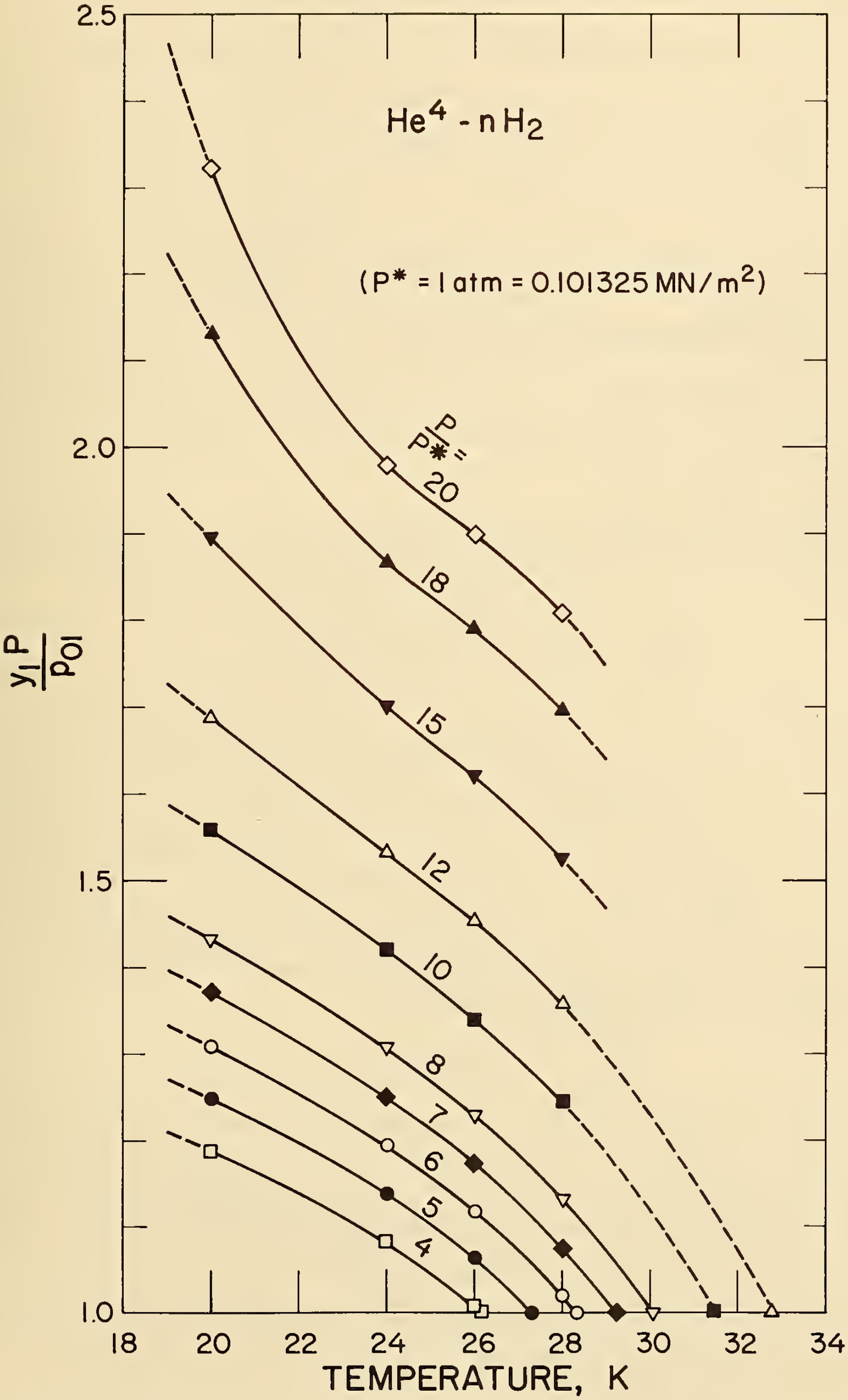

Figure 18. Enhancement factors for the He^4-nH_2 system at constant system pressure.

uncertainty in the measurements and the knowledge of the vapor pressure), though there is no theoretical reason why values less than unity cannot occur.

Enhancement factors for the He^4 - nH_2 system are shown in figure 17, and cross-plots are shown in figure 18. The 29 K isotherm shown in figure 17 was determined by extrapolation. Based on the experimental results of the nD_2 systems, these enhancement factors also are considered representative of those for the He^3 - nH_2 system within the pressure and temperature limits of this investigation.

D. Derived K-values and Heats of Solution.

The graphs of Henry's law values and enhancement factor values provide a convenient form for smoothing and interpolating the experimental data. These graphs were used to obtain smoothed liquid and vapor phase compositions and K-values, i.e., ratios of vapor phase to liquid phase mole fractions for each component, at even increments of system pressure. The essential values for He are given in tables 10 and 11 for the nD_2 and nH_2 systems, respectively.

The heat of solution for He dissolving in liquid nD_2 or nH_2 can be calculated directly from the He^4 and He^3 K-values from the integrated expression[41]

$$\Delta H_s = R[T'T/(T' - T)] \ln(K_2/K_2') \qquad (4)$$

postulating ideal solution. These values are listed in table 12 for all four systems.

The heats of solution for He^4 in liquid nH_2, with the exception of those at the highest temperatures, all fall within 400 - 800 J/mol (endothermic) in the agreement with the estimate of Corruccini.[18] The increase in heat of solution with temperature for all four systems is also consistent with the behavior of the He - CH_4,[42] H_2 - C_2H_6,[43] and H_2 - C_2H_4[44] systems studied earlier. It should be noted that the sign of heat of solution values for the He - CH_4 and H_2 - C_2H_6 were erroneously reported as negative; i.e., heats of solution for all of these systems are endothermic.

4. Discussion

A. Maxima in Gas Solubility at Constant System Pressure.

In systems of the type studied here, the solubility of the gas in a liquid solvent can pass through a maximum at constant system pressure (below the solvent critical pressure) as temperature is increased; thence the solubility must decrease toward zero as the temperature approaches the saturation temperature of the solvent at the subject pressure. Liquid phase compositions for the He^4 - nD_2 and He^3 - nD_2 systems at constant system pressure are shown in figure 19.

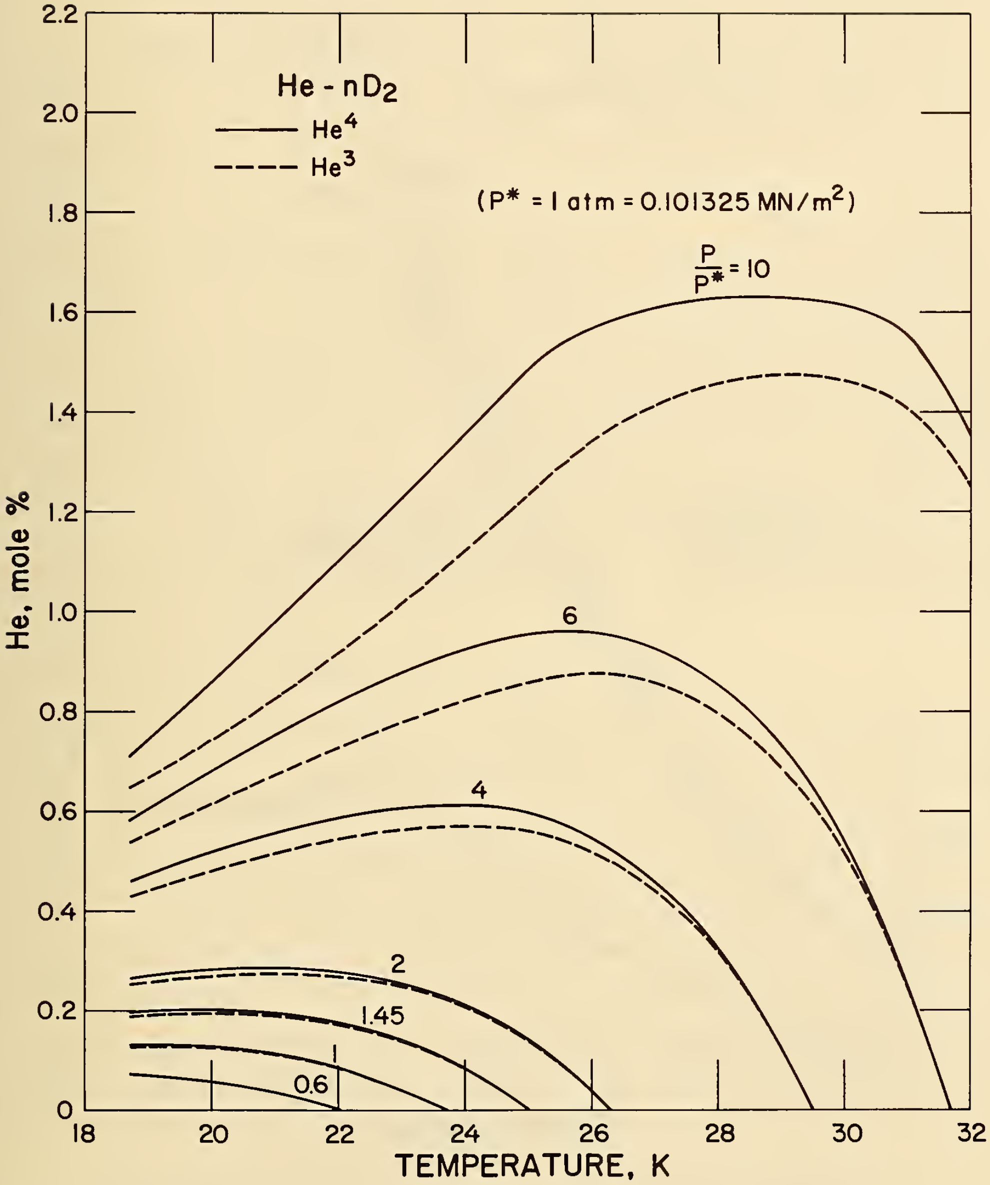

Figure 19. Solubility of He^4 and He^3 in liquid nD_2 at constant system pressure.

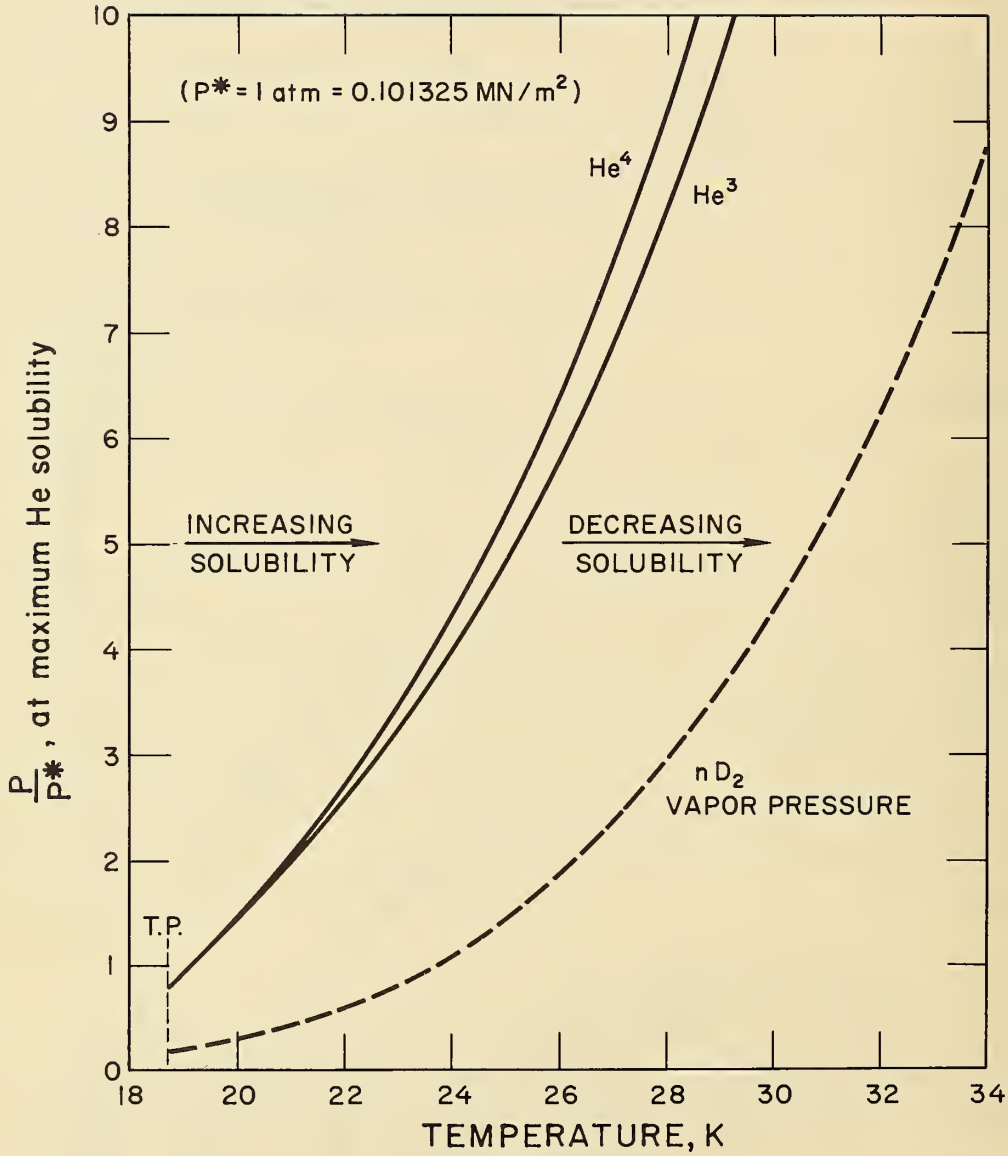

Figure 20. Solubility maxima for He^4 and He^3 in liquid nD_2.

Maxima are apparent in all of the isobars with the exception of that for $P/P^* = 0.6$, even though the data are extrapolated to the triple point temperature of nD_2. Though the temperatures associated with the maxima cannot be determined with a high degree of certainty, it appears that the He^3 maxima occur at slightly higher temperatures, but are essentially the same at the lowest temperature. The loci of solubility maxima for the $He^4 - nD_2$ and $He^3 - nD_2$ systems are shown in figure 20 along with the vapor pressure curve for nD_2. This figure serves as a 'map' for regions of increasing and decreasing solubility. A significant point worth noting is that the region below $P/P^* = 0.75$, bounded by the three phase locus (melting line) and the vapor pressure curve of nD_2, is one in which no solubility maxima exist; i.e., solubility always decreases with increasing temperature at fixed system pressure in this region.

Similarly, the $He^4 - nH_2$ and $He^3 - nH_2$ systems exhibit maxima in gas solubility at constant system pressure. Liquid phase compositions at constant system pressure for these systems are shown in figure 21. Since the data of the present investigation do not extend much below the normal boiling point of nH_2 complete information on solubility maxima cannot be obtained. The data of Streett et al.[10] are included in figure 21 below the lower temperature limit of the present measurements to indicate the qualitative dependence of solubility in this region and to provide a comparison between the two sets where the largest disagreement was found. This disagreement is about twice the estimated uncertainty of the present data.

B. Deficiency of Predictions from Regular Solution Theory.

It would be desirable, of course, to find the source of the discrepancy between the data of Streett et al.[10] and the present data or to show, through sound theoretical argument, which data are closer to the true values. The method of calculating gas solubility in a liquid solvent used by Corruccini,[18] which was adapted by Prausnitz[45] from regular solution theory, provides a good example of the difficulty one encounters in applying theory to evaluate such discrepancies. The steps followed in the solution process are: (1) compression of the solute gas from its partial pressure to an isometric mixing pressure at which its molar volume is equivalent to its partial molar volume in solution, (2) dissolving the gas in the liquid at the isometric mixing pressure, and (3) decompression of the liquid solution to the final system pressure. The equation for this process is

$$- \ln x_2 = \ln[f_2(\pi)/f_2(\bar{P}_2)] + \bar{v}_2 \varphi_1^2 (\delta_2 - \delta_1)^2/RT + (1/RT)\int_{\pi}^{P} \bar{v}_2 \, dP . \quad (5)$$

In the second term, the volume fraction, φ_1, for these systems is quite close to unity, and the product of the partial molar volume and the square of the difference of solubility parameters is representative of the heat of solution.

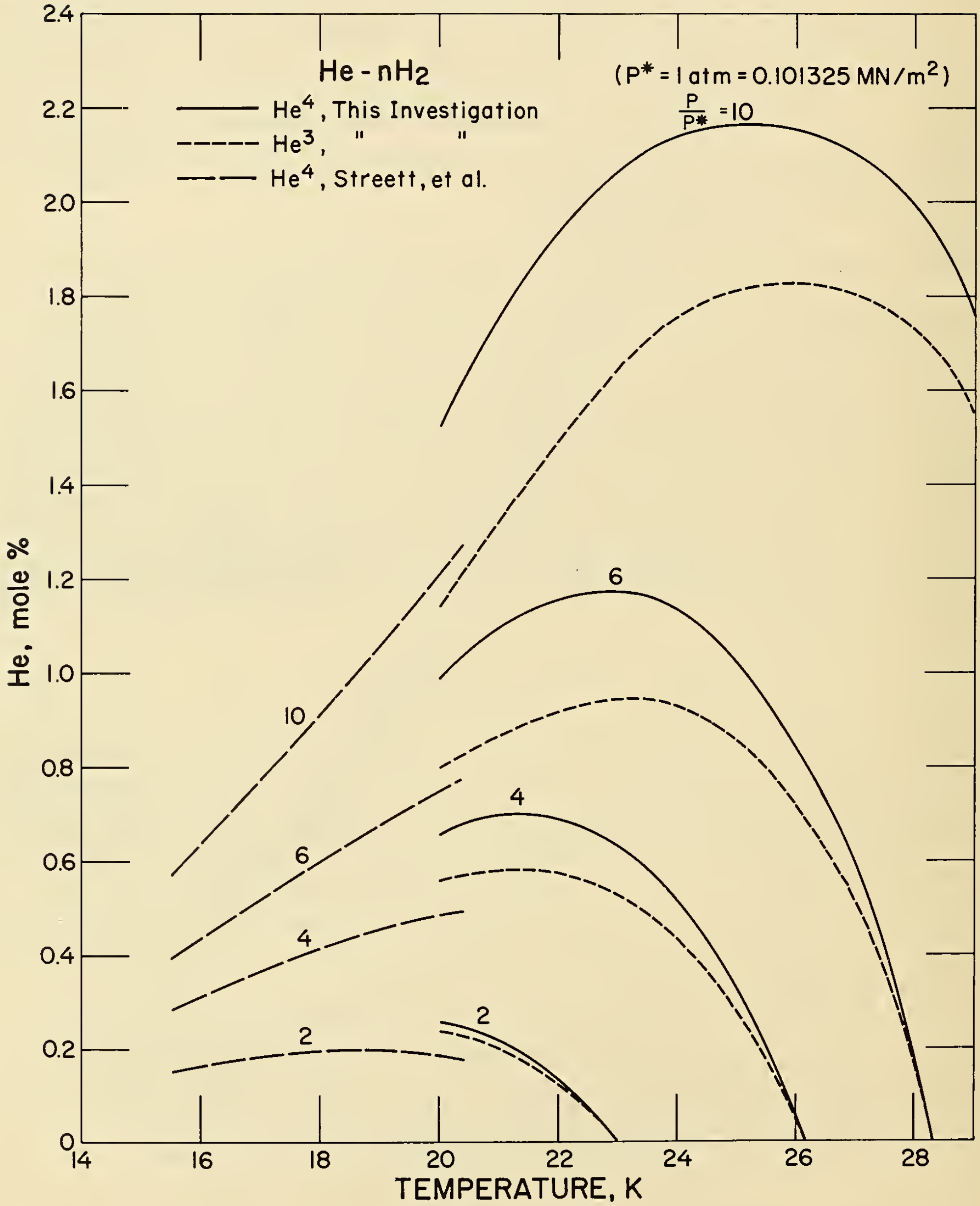

Figure 21. Solubility of He^4 and He^3 in liquid nH_2 at constant system pressure.

Equation (5) was used in this study to determine $\bar{v}_2$, the partial molar volume of He^4, and π, the related isometric mixing pressure, needed to reproduce the present experimental mole fraction of He^4 in liquid nH_2 at 20 K for $P/P^* = 10$. With this information, an attempt was made to estimate the relative solubility of He^3 in nH_2 and He^4 in nD_2 at the same conditions of temperature and pressure. The necessary PVT and thermodynamic properties for He^4, He^3, D_2, and H_2 were taken from McCarty,[24] Gibbons and Nathan,[25] Prydz,[23] and Roder, Weber, and Goodwin,[46] respectively. The latter reference is a convenient source of pH_2 rather than nH_2 properties; but, as will be shown later, the difference has no significant effect on the phase equilibrium properties of these systems in the region of consideration.

Briefly, it was found that for the He^4-nH_2 system, $\bar{v}_2 = 34.67\ cm^3/gmol$ and $\pi = 60$ atm ($6.0\ MN/m^2$) resulted in $x_2 = 0.0145$ at 20 K for $P/P^* = 10$, compared to the experimental value of $x_2 = 0.0153$ from the present measurements. Using $\bar{v}_2 = 39.20\ cm^3/gmol$ and $\pi = 50$ atm ($5.0\ MN/m^2$) resulted in $x_2 = 0.0109$, in closer agreement with the experimental value of Streett et al.[10] of $x_2 = 0.0121$. Corruccini's[18] estimate of $\bar{v}_2$ from the volume of solid He^4 would fall between these values, but probably closer to the value needed to reproduce the data of Streett et al. However, the uncertainty in Corruccini's estimate of $\bar{v}_2$ is at least ± 10%, which makes agreement with either set of data possible.

For the He^3-nH_2 system, a partial molar volume was estimated by adjusting the He^4 molar volume of $34.67\ cm^3/gmol$ with the ratio of He^3 to He^4 liquid phase molar volumes. This results in a value of about $54.00\ cm^3/gmol$ and an isometric mixing pressure of 35 atm ($3.5\ MN/m^2$). The result of $x_2 = 0.00074$ obtained with these parameters is quite disappointing. Using the same isometric mixing pressure as that for He^4 and the corresponding molar volume for He^3, $37.24\ cm^3/gmol$, results in $x_2 = 0.0044$; alternatively, using approximately the same molar volume as for He^4, $34.06\ cm^3/gmol$, and the corresponding isometric mixing pressure for He^3, 70 atm ($7.0\ MN/m^2$), results in $x_2 = 0.0058$. The experimental values are $x_2 = 0.0114$ from the present investigation at 20 K for $P/P^* = 10$, and $x_2 = 0.0103$ from the measurements of Matyash et al.[16] at 20.4 K for $P/P^* = 10.2$.

Though the prediction of He^3 solubility was not successful, one might expect to obtain better results in predicting the solubility of He^4 in nD_2 using the parameters that seem to work for He^4 in nH_2. The solvent effect is only introduced in the solubility parameter term. However, $x_2 = 0.00077$ is obtained with these parameters compared to the experimental value of $x_2 = 0.0086$ at 20 K for $P/P^* = 10$. This strongly suggests that Corruccini's success in estimating reasonable solubility limits for the He^4-nH_2 system was fortuitous. Further discussion or development of theory for systems of this type is

beyond the scope of this paper. It is hoped that this subject can be explored in more detail in the near future. The remainder of the discussion in this paper will be restricted to comparisons with data of previous investigators through Henry's law values from the liquid phase data and enhancement factors from the vapor phase data, in that order.

C. Comparisons of the Liquid Phase Data for the He - H_2 Systems.

Henry's law values from the three liquid phase isotherms of Smith[9] for the He^4 - nH_2 system are compared in figure 22 with those for two isotherms, 20.4 and 21.7 K, interpolated from the present data. The 21.7 K isotherm of Smith is quite erratic and is in poor agreement with the present data, as well as being inconsistent with his other two isotherms. The 20.4 K isotherm, on the other hand, appears well behaved and is in reasonable agreement at the higher pressures with the comparable isotherm taken from the present data. Smith's 17.4 K isotherm is difficult to compare directly with the data of the present investigation in other than a qualitative way. However, a comparison can be made relative to the data of Streett et al.[10] The He^4 compositions in the liquid phase at 17.4 K reported by Smith are lower than those reported by Streett et al. by 30 - 50%, in the pressure range of the present investigation, the worst agreement being at the lower pressures. As shown in figure 21, the He^4 compositions reported by Streett et al. are about 20% lower than those of this investigation at 20 K; on the other hand, Smith's He^4 compositions are a few percent higher than those of Streett et al. at 20.4 K, particularly at the higher pressures.

Six of the liquid phase data points of Roellig and Giese[12] for the He^4 - H_2 system, approximately equivalent to two isotherms, are compared in figure 23 with corresponding isotherms taken from the present investigation. The temperatures for the Roellig and Giese data are those calculated by Eckert and Prausnitz.[17] It is presumed that these data are for pH_2, since the authors used the vapor pressure curve of Chelton and Mann[47] in calculating the temperatures they originally reported. The same pH_2 vapor pressure curve also was used here to determine the Henry's law values of the Roellig and Giese data shown in figure 23. Though it is not possible to draw reasonable curves through the data points of Roellig and Giese, it is clear that both partial pressure and temperature dependence of their Henry's law values are exactly opposite to the partial pressure and temperature dependence of those from this investigation.

Three liquid phase isotherms, representative of the data reported in separate University of Michigan investigations, are compared in figure 24 with corresponding isotherms taken from the present investigation. For practical purposes, the University of Michigan data can be taken as one complete set for the He^4 - nH_2 system, covering a wide range of pressure, and for the He^4 - pH_2 system, covering the lower pressure range.

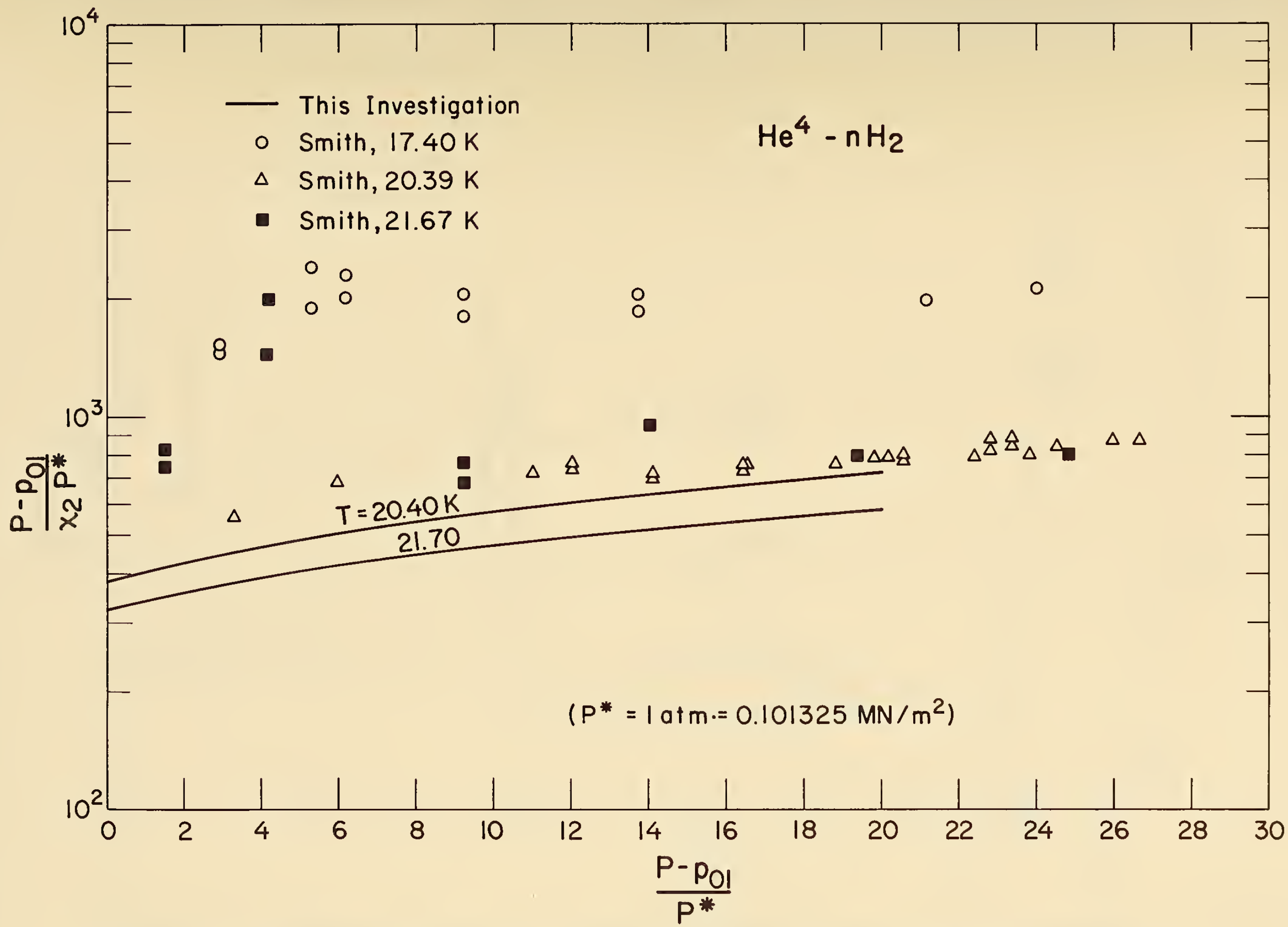

Figure 22. Henry's law values from the He^4-nH_2 data of Smith compared with those of this investigation.

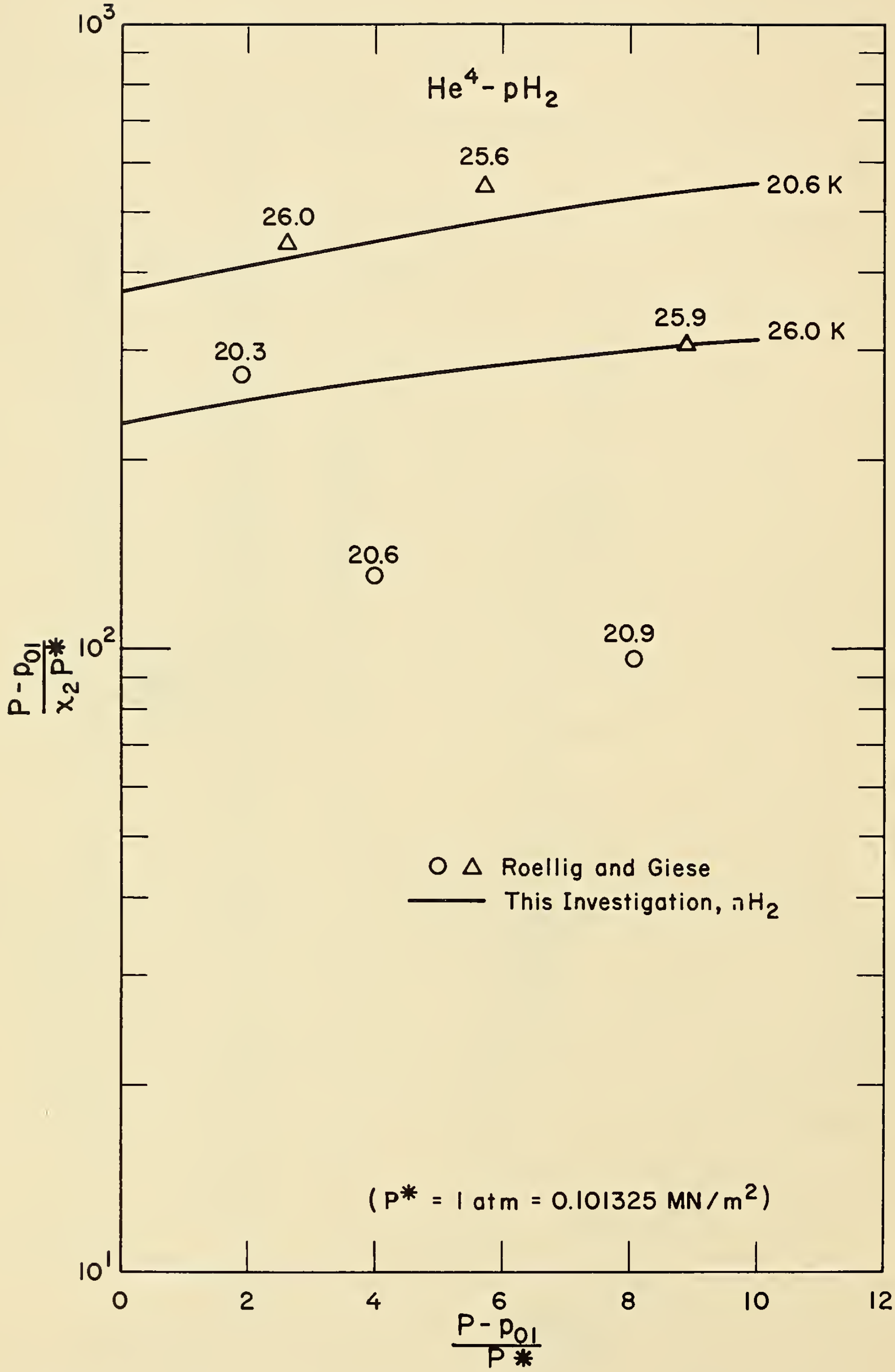

Figure 23. Henry's law values from the He^4-pH_2 data of Roellig and Giese compared with those for He^4-nH_2 from this investigation.

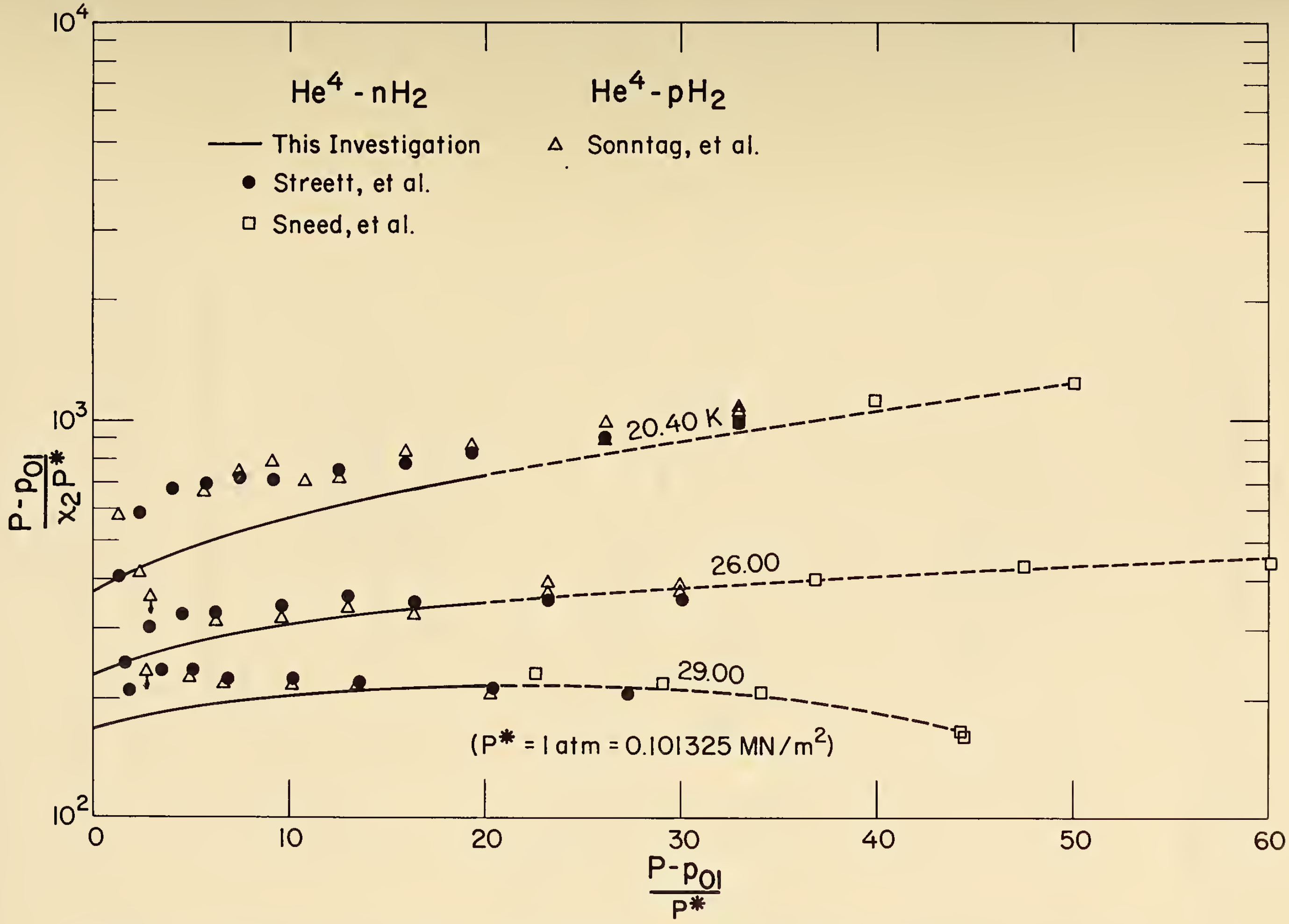

Figure 24. Henry's law values from the He^4-nH_2 data of Streett et al. and Sneed et al. and from the He^4-pH_2 data of Sonntag et al. compared with those for the He^4-nH_2 data from this investigation.

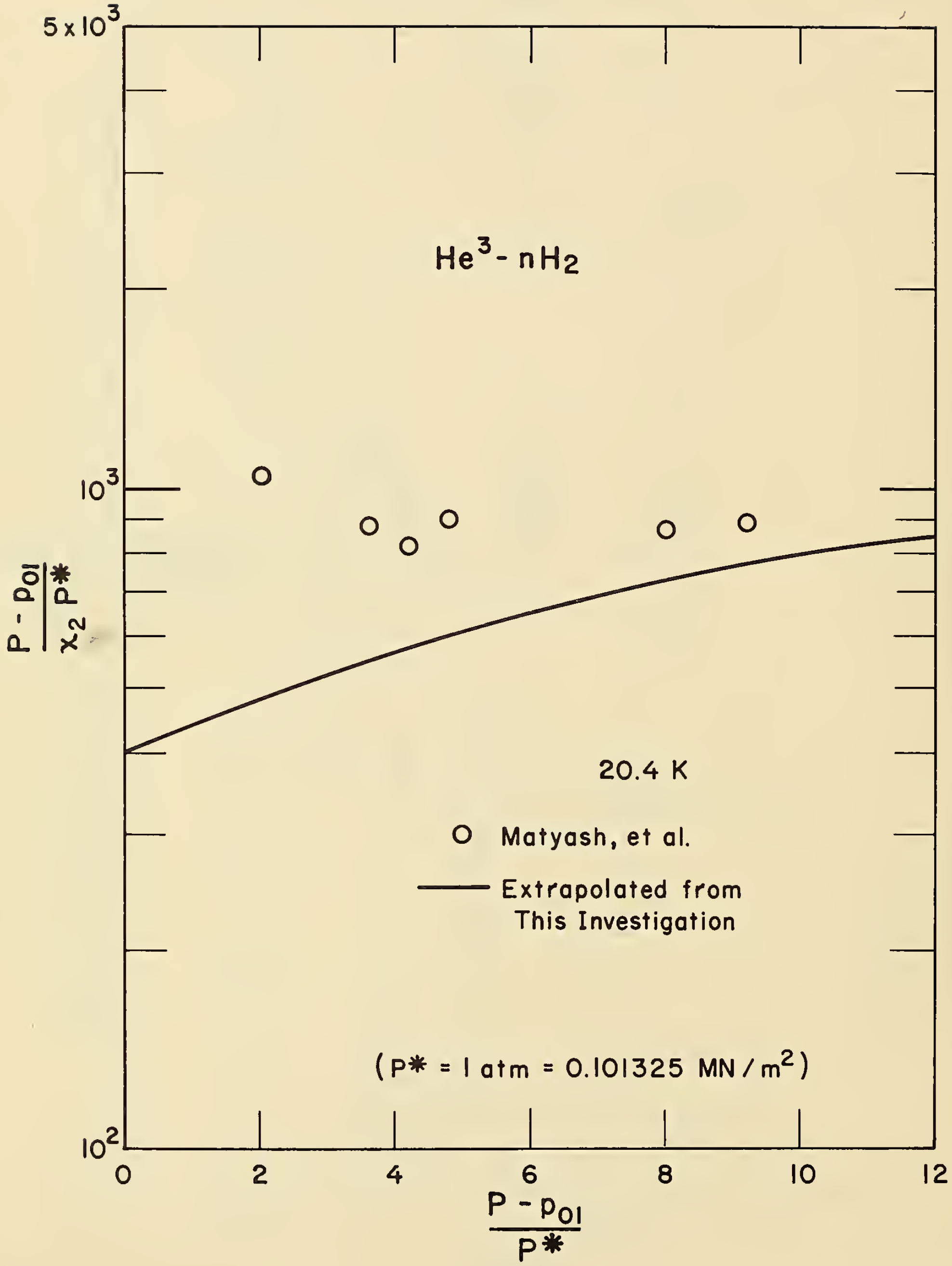

Figure 25. Henry's law values from the He^3-nH_2 data of Matyash et al. compared with those of this investigation.

The apparatus used in each was developed by Streett, and all compositions were analyzed by mass spectrometry. Disagreement with the isotherms from the present investigation is largest in the low pressure region where low He^4 concentrations are encountered. It appears, however, that the isotherms of the present investigation would extrapolate to higher pressures in reasonably good agreement with the data of Sneed et al.[11] There is no significant difference indicated between the pH_2 data of Sonntag et al.[13] and the nH_2 data of Streett et al.[10] and Sneed et al.

One additional point to be noted in figure 24 is the steep, downward curvature of the Henry's values of Streett et al. as infinite dilution is approached. In fact, the lowest pressure values are in excellent agreement with those taken from the present investigation. With such extreme curvature, it is not clear how one should extrapolate the values of Streett et al. to infinite dilution. This is precisely the reason Staveley's[21] heats of solution, calculated from the infinite dilution Henry's constants, were less certain for the He^4-H_2 system than for other systems examined. In essence, Staveley, as well as Solen, Chueh, and Prausnitz,[48] disregard the lowest pressure values in making this extrapolation. The paper of Solen et al. presents a correlation of He solubility in several cryogenic solvents, with special attention to predicting He solubility in mixed solvents.

Finally, the liquid phase isotherm at 20.4 K of Matyash, Mank, and Starkov[16] for the He^3-H_2 system is compared in figure 25 with the corresponding isotherm extrapolated from the present data. The ortho-para form of H_2 was not specified by the above authors, but it was presumed here to be nH_2. As found in previous comparisons, the largest disagreement occurs at the lower pressures, and the difference decreases as the pressure increases. The largest disagreement is about twice that between the data of Streett et al. and those of the present investigation for the He^4-nH_2 system. The data of Matyash et al. indicate that the Henry's law values are essentially constant in this pressure range and are equivalent to the infinite dilution value. Qualitatively, this behavior is not consistent with that for the He^4-nH_2 system, and certainly is not in agreement with the behavior of the data from the present investigation. Their infinite dilution Henry's constant would be about twice that obtained from the present investigation.

D. Comparisons of the Vapor Phase Data for the He^4-H_2 Systems.

Enhancement factors from the three vapor phase isotherms of Smith[9] for the He^4-nH_2 system and corresponding isotherms taken from the present investigation are compared in figure 26. The 17.4 K curve taken from the present investigation is only an approximation; however, the extrapolation at the low pressures is not difficult and the results should be reasonably correct. The 17.4 K isotherm of Smith, with the exception of two low pressure points, appears to be consistent with the present data, but is somewhat higher. The tendency for the lower temperature enhancement factor curves to

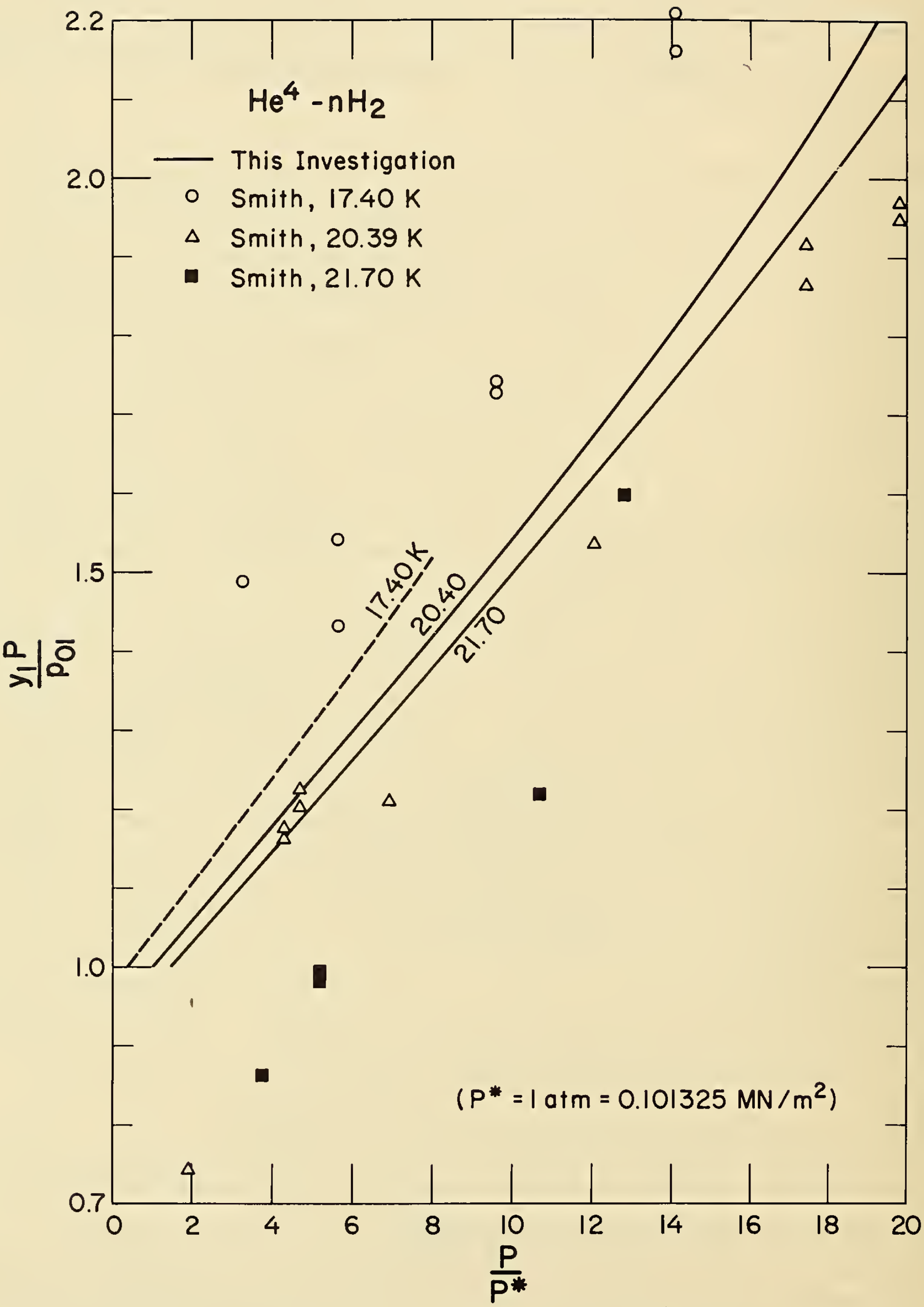

Figure 26. Enhancement factors from the He^4-nH_2 data of Smith compared with those of this investigation.

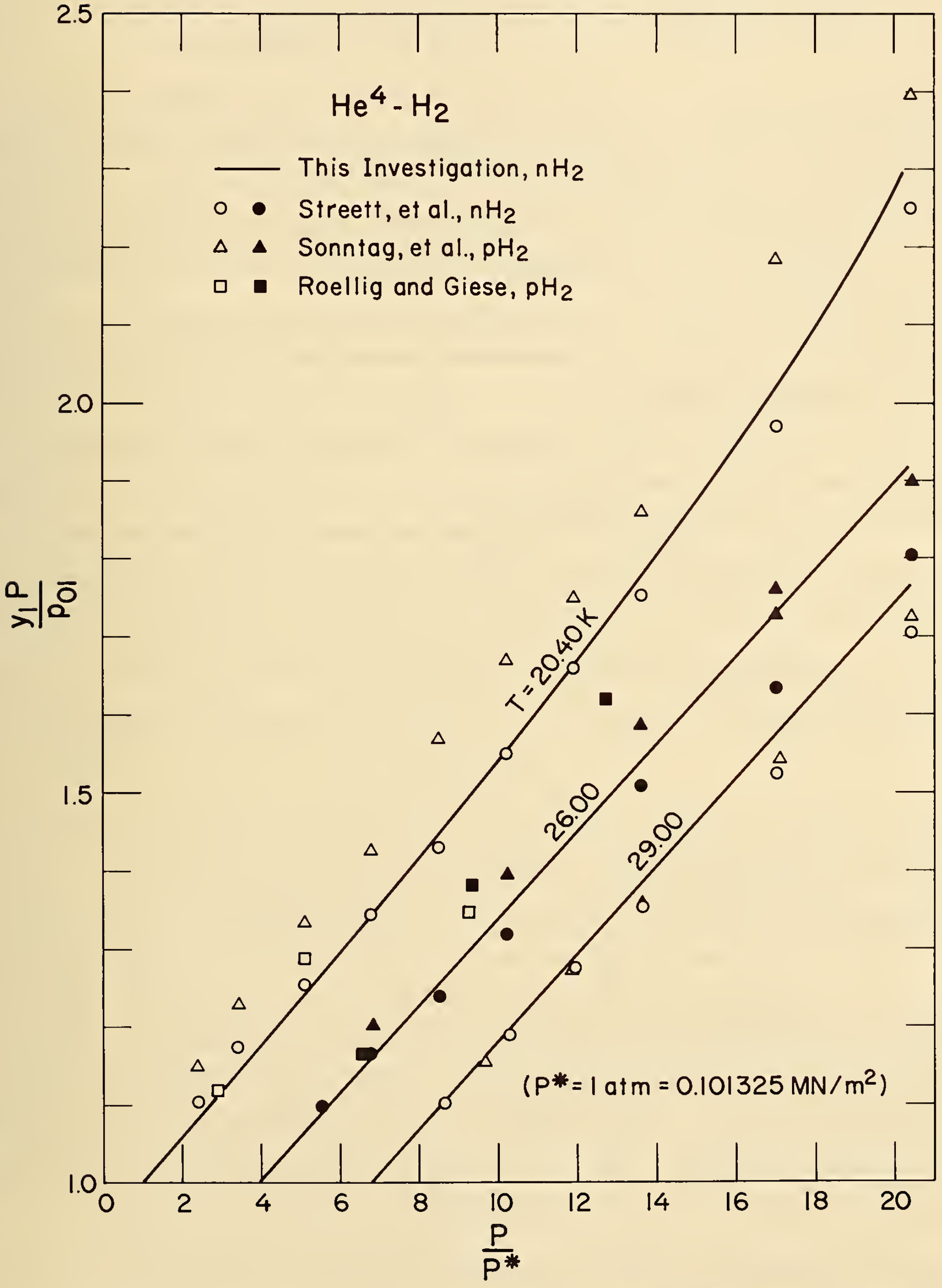

Figure 27. Enhancement factors from the He^4-nH_2 data of Streett et al. and from the He^4-pH_2 data of Sonntag et al. and of Roellig and Giese compared with those for He^4-nH_2 from this investigation.

increase in slope as pressure increases, as Smith's 17.4 K isotherm does, is consistent with the behavior observed in this investigation. If the one point with an enhancement factor of 0.74 were disregarded, the 20.4 K isotherm of Smith would be fairly well behaved. However, the behavior of his 21.7 K isotherm is simply incorrect. Since the Henry's law values for the liquid phase are high and the enhancement factors for the vapor phase are low, Smith's reported temperature of 21.7 K might be erroneously high.

Enhancement factors from vapor phase isotherms representative of the data of Streett et al.[10] for the He^4-nH_2 system, of Sonntag et al.[13] for the He^4-pH_2 system, and the corresponding isotherms taken from the present investigation are compared in figure 27. Enhancement factors from the six vapor phase points of Roellig and Giese,[12] equivalent to two isotherms at approximately 20.6 and 25.8 K, are also shown. Agreement between the present data and those of the University of Michigan investigators is excellent; differences in the enhancement factors are generally less than 3% at the higher temperatures. At the lowest temperature agreement is not quite so good; however, the largest disagreement is less than 7%. With the exception of the one high pressure point at 20.6 K, the vapor phase data of Roellig and Giese appear to be in reasonable agreement with the present data. Of the five remaining points the largest disagreement is about 8.4%.

There may be slight differences between the enhancement factors for pH_2 and for nH_2, as indicated by an increasing difference between the data of Sonntag et al. and Streett et al. with decreasing temperature. However, since the uncertainty also increases with decreasing temperature, the apparent difference is not considered significant.

5. Summary

This investigation provides new data for two systems, He^4-nD_2 and He^3-nD_2, which had not been studied previously. These data were extrapolated down to the triple point temperature of nD_2, 18.72 K, and up to 32 K. Measurements in the liquid-vapor region for the He^3-nH_2 system, though not made to as low a reduced temperature as that for the nD_2 systems, provide the major portion of all data now available for that system. The data obtained for the He^4-nH_2 system serve as comparative reference to results of several other experimental investigations covering a wide range of temperature and pressure. The measurements of nD_2 and nH_2 vapor pressures not only provide verification of the experimental technique, but help to point out an explainable discrepancy in the nD_2 vapor pressure values, a fact of which this author was previously unaware.

Based on the evaluation of these results and comparisons with other data, the following conclusions can be drawn.

1) The present measurements provide a consistent set of data on the relative phase equilibrium properties of the He^4-nD_2, He^3-nD_2, He^4-nH_2, and He^3-nH_2 systems. Though efforts were made to avoid systematic errors, if such an error is present it will be reflected in the data for all four systems. The uncertainty in composition determination, the largest source of error in this investigation, is estimated to be ± 3% of the concentration of the minor component, or ± 0.1 mole %, whichever is greater.

2) There is no apparent difference in the equilibrium vapor phase compositions between the He^4-nD_2 and He^3-nD_2 systems, within the pressure and temperature limits of this investigation. Thus, none is expected between the He^4-nH_2 and He^3-nH_2 systems. There is, however, a significant difference between the solubility limits of He^4 and He^3 in the liquid phase, the ratio of which is about the same in both liquid solvents.

3) There is a significant difference in both the liquid and vapor phase compositions between the nD_2 and nH_2 systems, even at the same nD_2 and nH_2 reduced temperature; i. e., 30 and 26 K, respectively. At the same absolute temperature, the differences are quite pronounced. The solubility of He^4 in liquid nD_2 and the enhancement factor of nD_2 in He^4 are both lower than the corresponding nH_2 values. Data from the University of Michigan studies[10, 13] indicate no apparent difference in the phase equilibrium properties between the normal and para H_2 forms; thus, none is expected between the normal and ortho D_2 forms.

4) Though the disagreement between the He^4-nH_2 and He^4-pH_2 liquid phase data of the University of Michigan investigators[10, 11, 13, 14] and comparable data from the present investigation for He^4-nH_2 is somewhat larger in the low pressure region than the present estimates of uncertainty, these former measurements provide the most complete and, for the most part, reasonably consistent set of data for the He^4-nH_2 and He^4-pH_2 systems. The earlier data of Smith[9], though valuable as pioneering work, and the subsequent data of Roellig and Giese[12] are too limited and inconsistent to be of further value.

5) The data of Matyash et al.[16] for the solubility of He^3 in liquid H_2, in addition to the University of Michigan data on the solubility of He^4 in liquid H_2, support the results of the present investigation; i. e., the solubility of He^3 is less than that of He^4. The disagreement between the data of Matyash et al. and the present data is significantly larger in the lower pressure region than that observed between the University of Michigan data and those of the present investigation for He^4. In each case, however, the disagreement is in the same direction. Since Matyash et al. do not discuss the uncertainties in their measurements, it is not possible to further evaluate the disagreement noted.

6) Finally, prediction of the solubility of He^4 or He^3 in liquid nD_2 or liquid nH_2, using regular solution theory, is not promising. It is felt that the present data should be first correlated, possibly with a technique similar to that used by Solen et al.[48] The correlation could then be studied for clues to the nature of the deficiency of theory. In this respect, the prediction method discussed by Miller[49] should be examined more closely for possible application to quantum fluid mixtures.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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Table 1. Vapor Pressure of nD_2

$\ell n\ p_o\ (\text{atm}) = 7.987864211 - (221.2539491)/(4.032572130 + T)$

T K	p_o^* atm	p_o CALC atm	DIFF atm
20.000	0.2906	0.2957	-0.00506
21.000	0.4219	0.4271	-0.00518
22.000	0.6002	0.5997	0.00046
23.000	0.8302	0.8213	0.00889
24.000	1.1057	1.0998	0.00591
25.000	1.4433	1.4434	-0.00007
26.000	1.8645	1.8603	0.00421
27.000	2.3510	2.3587	-0.00775
28.000	2.9430	2.9468	-0.00377
29.000	3.6303	3.6321	-0.00180
30.000	4.4094	4.4221	-0.01274
32.000	6.3351	6.3438	-0.00869
34.000	8.7881	8.7616	0.02650
23.666		1.0000	

Standard Deviation = 0.010963

* 1 atm = 0.101325 MN/m^2

Table 2. Vapor Pressure of nH_2

$\ell n\ p_o\ (\text{atm}) = 7.987748573 - (219.6811229)/(7.127745367 + T)$

T K	p_o^* atm	p_o CALC atm	DIFF atm
20.000	0.8948	0.8956	-0.00079
21.000	1.1942	1.1944	-0.00018
22.000	1.5617	1.5617	0.00002
23.000	2.0108	2.0059	0.00490
24.000	2.5313	2.5354	-0.00408
25.000	3.1607	3.1582	0.00248
26.000	3.8820	3.8823	-0.00025
27.000	4.7122	4.7149	-0.00268
28.000	5.6546	5.6631	-0.00849
29.000	6.7400	6.7333	0.00665
30.000	7.9342	7.9316	0.00264
20.375		1.0000	

Standard Deviation = 0.0047181

* 1 atm = 0.101325 MN/m^2

Table 3. Experimental Liquid Phase Compositions for the He^4-nD_2 System

T K	P* atm	x_2 (He^4)	$\frac{P-p_{o1}}{x_2}$ atm
20.00	0.2906	0	
	9.717	0.0085^{5}	1103
	13.245	0.0092^{6}	1399
	16.719	0.0099^{7}	1648
	19.196	0.0101	1872
22.00	0.6002	0	
	8.404	0.0099^{2}	787
	10.227	0.0106	908
	13.909	0.0133	1001
	17.059	0.0136	1208
	19.801	0.0154	1247
24.00	1.1057	0	
	8.598	0.0126	594
	10.500	0.0143	659
	13.660	0.0157	801
	16.903	0.0195	809
	19.992	0.0200	943
26.00	1.8645	0	
	8.530	0.0146	457
	9.207	0.0142	519
	11.911	0.0182	551
	13.800	0.0200	596
	17.148	0.0212	721
	19.407	0.0252	695
	19.890	0.0247	730
28.00	2.9430	0	
	6.716	0.0103	367
	7.019	0.0109	373
	10.159	0.0148	487
	15.259	0.0236	521
	18.549	0.0278	562
	18.903	0.0277	577
	19.754	0.0292	577
30.00	4.4094	0	
	8.826	0.0136	325
	11.452	0.0192	367
	14.024	0.0249	386
	16.277	0.0290	409
	20.400	0.0367	436
	20.414	0.0341	470

* 1 atm = 0.101325 MN/m^2

Table 4. Experimental Liquid Phase Compositions for the He^3-nD_2 System

T K	P* atm	x_2 (He^3)	$\frac{P-p_{o1}}{x_2}$ atm
20.00	0.2906	0	
	3.450	0.0065^{2}	485
	6.162	0.0062^{6}	938
	9.295	0.0065^{3}	1379
	11.704	0.0083^{2}	1372
	14.446	0.0086^{3}	1640
22.00	0.6002	0	
	5.012	0.0072^{5}	609
	7.454	0.0083^{5}	821
	9.595	0.0086^{8}	1036
	12.269	0.0090^{5}	1289
	16.124	0.0104	1500
24.00	1.1057	0	
	4.018	0.0060^{5}	481
	5.655	0.0074^{1}	614
	6.492	0.0091^{5}	589
	8.724	0.0098^{1}	777
	9.098	0.0107	744
	9.220	0.0109	744
	11.153	0.0114	879
	13.589	0.0118	1057
	13.745	0.0124	1023
26.00	1.8645	0	
	5.740	0.0090^{8}	427
	6.948	0.0106	481
	8.604	0.0122	554
	11.200	0.0142	659
	15.446	0.0170	800
28.00	2.9430	0	
	9.343	0.0122	525
	11.721	0.0158	555
	14.814	0.0187	634
30.00	4.4094	0	
	8.986	0.0130	353
	10.517	0.0155	394
	13.357	0.0192	466
	17.583	0.0257	513

* 1 atm = 0.101325 MN/m^2

Table 5. Experimental Liquid Phase Compositions for the He^4-nH_2 System

T K	P^* atm	x_2 (He^4)	$\frac{P-p_{o1}}{x_2}$ atm
20.00	0.8948	0	
	7.250	0.0110	580
	11.061	0.0172	592
	15.756	0.0211	703
	19.849	0.0244	776
22.00	1.5617	0	
	5.784	0.0107	394
	9.649	0.0204	397
	14.463	0.0266	485
	20.353	0.0343	548
24.00	2.5313	0	
	7.291	0.0155	307
	10.765	0.0231	357
	16.331	0.0333	414
	19.805	0.0411	421
26.00	3.8820	0	
	8.370	0.0150	299
	10.782	0.0238	290
	12.327	0.0283	299
	13.776	0.0307	322
	15.814	0.0373	320
	17.814	0.0430	324
	19.992	0.0471	342
28.00	5.6546	0	
	8.247	0.0141	184
	11.554	0.0267	221
	11.639	0.0264	227
	16.797	0.0458	243
	19.720	0.0566	249

* 1 atm = 0.101325 MN/m^2

Table 6. Experimental Liquid Phase Compositions for the He^3-nH_2 System

T K	P* atm	x_2 (He^3)	$\frac{P-p_{o1}}{x_2}$ atm
22.00	1.5617	0	
	8.189	0.0123	538
	10.462	0.0151	589
	13.545	0.0201	597
	14.936	0.0215	623
24.00	2.5313	0	
	7.863	0.0137	389
	10.238	0.0176	439
	12.623	0.0221	456
	14.783	0.0285	430
26.00	3.8820	0	
	7.723	0.0113	339
	10.299	0.0178	361
	13.443	0.0285	336
	15.174	0.0331	342
28.00	5.6546	0	
	9.179	0.0148	239
	11.547	0.0227	260
	13.000	0.0280	262
	15.205	0.0368	260

* 1 atm = 0.101325 MN/m^2

Table 7. Experimental Vapor Phase Compositions for the He^4-nD_2 System

T K	P^* atm	y_1 (nD_2)	$\frac{y_1 P}{P_{o1}}$
20.00	0.2906	1.00	1.00
	6.743	0.0602^9	1.399
	9.911	0.0457^5	1.560
	13.517	0.0392^2	1.824
	18.015	0.0348^9	2.163
24.00	1.1058	1.00	1.00
	3.984	0.3143	1.132
	8.342	0.1760	1.328
	14.035	0.1217	1.545
	20.172	0.1005	1.833
28.00	2.9430	1.00	1.00
	7.992	0.4436	1.205
	10.503	0.3688	1.316
	15.538	0.2884	1.523
	19.039	0.2523	1.632
30.00	4.4094	1.00	1.00
	7.148	0.6905	1.119
	10.418	0.5335	1.260
	15.229	0.4127	1.425
	20.009	0.3556	1.614

* 1 atm = 0.101325 MN/m^2

Table 8. Experimental Vapor Phase Compositions for the He^3-nD_2 System

T K	P^* atm	y_1 (nD_2)	$\frac{y_1 P}{P_{o1}}$
20.00	0.2906	1.00	1.00
	5.217	0.0725^3	1.302
	5.590	0.0694^2	1.335
	8.441	0.0511^7	1.486
	12.439	0.0402^5	1.723
	15.637	0.0358^7	1.930
24.00	1.1058	1.00	1.00
	3.634	0.3499	1.150
	8.234	0.1798	1.339
	12.340	0.1365	1.523
	15.834	0.1154	1.653
28.00	2.9430	1.00	1.00
	8.693	0.4187	1.237
	12.242	0.3275	1.362
	14.412	0.2922	1.431
30.00	4.4094	1.00	1.00
	7.403	0.6741	1.132
	9.904	0.5469	1.228
	13.147	0.4458	1.329
	16.937	0.3808	1.463

* 1 atm = 0.101325 MN/m^2

Table 9. Experimental Vapor Phase Compositions for the He^4-nH_2 System

T K	P^* atm	y_1 (nH_2)	$\frac{y_1 P}{P_{o1}}$
20.00	0.8948	1.00	1.00
	6.151	0.1951	1.341
	10.278	0.1370	1.574
	14.865	0.1133	1.882
	19.029	0.1047	2.227
24.00	2.5313	1.00	1.00
	6.638	0.4699	1.232
	10.710	0.3457	1.463
	15.314	0.2839	1.718
	19.938	0.2494	1.964
26.00	3.8820	1.00	1.00
	8.621	0.5849	1.299
	12.027	0.4665	1.445
	16.076	0.4010	1.661
	19.699	0.3782	1.919
28.00	5.6546	1.00	1.00
	8.635	0.7741	1.182
	11.775	0.6460	1.345
	15.885	0.5626	1.580
	20.077	0.5091	1.808

* 1 atm = 0.101325 MN/m^2

Table 10. He^4 and He^3 K-values for the nD_2 Systems

T K	P* atm	x_2 He^4	x_2 He^3	K_2 He^4	K_2 He^3
19	2	0.00271	0.00258	329.5	346.1
	4	0.00475	0.00441	197.9	213.2
	6	0.00606	0.00556	157.7	171.9
	8	0.00688	0.00625	140.1	154.2
	10	0.00740	0.00667	130.9	145.2
	12	0.00767	0.00687	126.6	141.4
	14	0.00789	0.00692	123.4	140.6
	16	0.00802	0.00696	121.5	140.0
	18	0.00824		118.4	
	20	0.00856		114.0	
20	2	0.00285	0.00263	294.6	319.3
	4	0.00520	0.00473	175.2	192.6
	6	0.00675	0.00610	138.5	153.3
	8	0.00778	0.00703	121.7	134.7
	10	0.00855	0.00770	111.6	123.9
	12	0.00903	0.00815	106.2	117.6
	14	0.00943	0.00848	102.0	113.4
	16	0.00975	0.00878	98.88	109.8
	18	0.01002		96.37	
	20	0.01025		94.29	
22	2	0.00280	0.00275	242.1	246.5
	4	0.00595	0.00555	138.4	148.4
	6	0.00802	0.00728	108.7	119.8
	8	0.00958	0.00838	93.58	107.0
	10	0.01075	0.00905	84.75	100.7
	12	0.01182	0.00952	77.91	96.73
	14	0.01275	0.00985	72.78	94.21
	16	0.01360	0.01015	68.62	91.94
	18	0.01438		65.18	
	20	0.01518		61.94	
24	2	0.00215	0.00202	197.4	210.1
	4	0.00622	0.00565	110.4	121.6
	6	0.00955	0.00815	81.13	95.07
	8	0.01195	0.00975	68.53	83.99
	10	0.01375	0.01090	61.48	77.56
	12	0.01525	0.01180	56.62	73.17
	14	0.01660	0.01248	52.78	70.21
	16	0.01783	0.01300	49.68	68.14
	18	0.01898		47.06	
	20	0.02010		44.74	

* 1 atm = 0.101325 MN/m^2

Table 10. He^4 and He^3 K-values for the nD_2 Systems (continued)

T K	P^* atm	x_2 He^4	x_2 He^3	K_2 He^4	K_2 He^3
26	2	0.00040	0.00032	153.0	191.3
	4	0.00550	0.00525	89.11	93.35
	6	0.00982	0.00902	64.55	70.28
	8	0.01322	0.01158	53.46	61.04
	10	0.01585	0.01335	47.34	56.20
	12	0.01812	0.01485	43.02	52.49
	14	0.02005	0.01605	39.93	49.88
	16	0.02190	0.01715	37.28	47.61
	18	0.02362		35.10	
	20	0.02528		33.18	
28	4	0.00320	0.00312	71.78	73.62
	6	0.00853	0.00805	52.19	55.30
	8	0.01278	0.01142	43.39	48.56
	10	0.01612	0.01395	38.52	44.51
	12	0.01910	0.01603	34.83	41.50
	14	0.02185	0.01795	31.92	38.86
	16	0.02443	0.01965	29.54	36.73
	18	0.02692	0.02128	27.51	34.81
	20	0.02942		25.69	
30	6	0.00538	0.00525	39.72	40.70
	8	0.01118	0.01065	32.55	34.17
	10	0.01618	0.01458	28.20	31.30
	12	0.02062	0.01780	25.17	29.16
	14	0.02475	0.02070	22.79	27.25
	16	0.02862	0.02340	20.92	25.59
	18	0.03235	0.02600	19.34	24.07
	20	0.03588		18.05	
32	8	0.00640	0.00617	23.48	24.36
	10	0.01357	0.01251	19.63	21.29
	12	0.02009	0.01787	17.27	19.42
	14	0.02616	0.02248	15.50	18.03
	16	0.03179	0.02670	14.16	16.85
	18	0.03727	0.03054	13.11	16.00
	20	0.04257		12.05	

* 1 atm = 0.101325 MN/m^2

Table 11. He^4 and He^3 K-values for the nH_2 Systems

T K	P* atm	x_2 He^4	x_2 He^3	K_2 He^4	K_2 He^3
20	2	0.00250	0.00238	208.9	219.4
	4	0.00650	0.00559	112.9	131.3
	6	0.00980	0.00798	82.10	100.8
	8	0.01265	0.00985	66.37	85.24
	10	0.01515	0.01141	56.79	75.41
	12	0.01745	0.01290	50.09	67.76
	14	0.01950	0.01432	45.30	61.69
	16	0.02130		41.77	
	18	0.02295		38.95	
	20	0.02450		36.58	
22	2	0.00130	0.00120	153.5	166.3
	4	0.00690	0.00575	80.42	96.50
	6	0.01165	0.00915	57.79	73.58
	8	0.01585	0.01200	46.20	61.02
	10	0.01955	0.01470	39.25	52.20
	12	0.02285	0.01750	34.60	45.18
	14	0.02580	0.02040	31.29	39.57
	16	0.02860	0.02335	28.65	35.09
	18	0.03125		26.51	
	20	0.03375		24.75	
24	4	0.00530	0.00440	59.38	71.52
	6	0.01145	0.00935	43.30	53.03
	8	0.01675	0.01355	34.99	43.25
	10	0.02145	0.01755	29.86	36.50
	12	0.02580	0.02155	26.23	31.41
	14	0.02995	0.02595	23.47	27.08
	16	0.03390	0.03050	21.31	23.68
	18	0.03770		19.56	
	20	0.04140		18.10	
26	6	0.00825	0.00715	33.45	38.60
	8	0.01485	0.01240	27.14	32.51
	10	0.02095	0.01760	22.86	27.22
	12	0.02660	0.02340	19.92	22.65
	14	0.03205	0.02960	17.66	19.12
	16	0.03735	0.03625	15.88	16.36
	18	0.04255		14.44	
	20	0.04760		13.26	

* 1 atm = 0.101325 MN/m^2

Table 11. He^4 and He^3 K-values for the nH_2 Systems (continued)

T K	P* atm	x_2 He^4	x_2 He^3	K_2 He^4	K_2 He^3
28	6	0.00190	0.00160	20.37	24.19
	8	0.01175	0.01005	16.95	19.82
	10	0.02020	0.01745	14.65	16.96
	12	0.02795	0.02435	12.88	14.79
	14	0.03535	0.03190	11.50	12.75
	16	0.04280	0.04000	10.29	11.01
	18	0.05020		9.313	
	20	0.05770		8.463	
29	8	0.00720	0.00636	13.57	15.36
	10	0.01762	0.01545	11.77	13.42
	12	0.02725	0.02402	9.963	11.30
	14	0.03667	0.03270	8.759	9.823
	16	0.04562	0.04152	7.867	8.644
	18	0.05533		7.002	
	20	0.06314		6.530	

* 1 atm = 0.101325 MN/m^2

Table 12 Heats of Solution

T K	P^* atm	ΔH_s J/mol He^4-nD_2	He^3-nD_2	He^4-nH_2	He^3-nH_2
19-20	2	354	255		
	4	385	321		
	6	410	362		
	8	445	427		
	10	504	501		
	12	555	582		
	14	602	680		
	16	651	768		
	18	650			
	20	600			
20-22	2	359	473	564	507
	4	431	477	621	563
	6	443	451	642	576
	8	481	421	663	611
	10	503	379	676	673
	12	567	357	677	741
	14	617	339	677	812
	16	668	325	690	
	18	715		704	
	20	769		715	
22-24	2	448	351		
	4	496	437	666	658
	6	642	508	634	719
	8	684	532	610	756
	10	705	573	600	785
	12	701	613	608	798
	14	705	645	631	833
	16	709	658	650	863
	18	715		667	
	20	714		687	
24-26	2	661	243		
	4	556	686		
	6	593	784	670	824
	8	644	828	659	741
	10	678	836	693	761
	12	713	862	714	848
	14	724	887	738	903
	16	745	930	763	959
	18	761		787	
	20	775		807	

* 1 atm = 0.101325 MN/m^2

Table 12 Heats of Solution (continued)

T K	P* atm	ΔH_s J/mol He^4-nD_2	He^3-nD_2	He^4-nH_2	He^3-nH_2
26-28	4	655	719		
	6	643	726	1501	1414
	8	632	692	1425	1498
	10	624	706	1347	1432
	12	639	711	1320	1290
	14	678	756	1298	1226
	16	704	785	1313	1199
	18	737		1327	
	20	774		1359	
28-29	8			1502	1721
	10			1478	1581
	12			1736	1817
	14			1837	1761
	16			1810	1633
	18			1927	
	20			1751	
28-30	6	953	1070		
	8	1004	1227		
	10	1089	1230		
	12	1134	1232		
	14	1176	1239		
	16	1205	1262		
	18	1230	1288		
	20	1233			
30-32	8	1304	1351		
	10	1446	1538		
	12	1503	1622		
	14	1538	1648		
	16	1558	1668		
	18	1552	1630		
	20	1613			

* 1 atm = 0.101325 MN/m^2

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Experimental data are reported for the equilibrium liquid and vapor phase compositions of the He^4 - nD_2 and He^3-nD_2 systems from 20 to 30 K and the He^4-nH_2 and He^3-nH_2 systems from 20 to 28 K. The maximum experimental pressures were 20 and 16 atm (2.0 and 1.6 MN/m^2) for the He^4 and He^3 systems, respectively. In addition, vapor pressures were measured from 20 to 34 K for nD_2 and from 20 to 30 K for nH_2.

Values of Henry's constants, enhancement factors, K-values, and heats of solution were derived from the experimental data for each system. The derived properties are compared with those derived from previous data for the He^4-nH_2, He^4-pH_2, and He^3-nH_2 systems.

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